Enhanced Control of Mercury by Wet Flue Gas Desulfurization Systems

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ABSTRACT

The U.S. Department of Energy and EPRI co-funded this project to improve the control of mercury emissions from coal-fired power plants equipped with wet flue gas desulfurization (FGD) systems. The project has investigated catalytic oxidation of vapor-phase elemental mercury to a form that is more effectively captured in wet FGD systems. If successfully developed, the process could be applicable to over 90,000 MW of utility generating capacity with existing FGD systems, and to future FGD installations.

Field tests were conducted to determine whether candidate catalyst materials remain active towards mercury oxidation after extended flue gas exposure. Catalyst life will have a large impact on the cost effectiveness of this potential process. A mobile catalyst test unit was used to test the activity of four different catalyst materials for a period of up to six months each at three utility sites. Catalyst testing was completed at the first site, which fires Texas lignite, in December 1998; at the second test site, which fires a Powder River Basin subbituminous coal, in November 1999; and at the third site, which fires a medium- to high-sulfur bituminous coal, in January 2001.

Results of testing at each of the three sites were reported in previous technical notes. At Site 1, catalysts were tested only as powders dispersed in sand bed reactors. At Sites 2 and 3, catalysts were tested in two forms, including powders dispersed in sand and in commercially available forms such as extruded pellets and coated honeycomb structures. This final report summarizes and presents results from all three sites, for the various catalyst forms tested.

Field testing was supported by laboratory tests to screen catalysts for activity at specific flue gas compositions, to investigate catalyst deactivation mechanisms and methods for regenerating spent catalysts. Laboratory results are also summarized and discussed in this report.

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EXECUTIVE SUMMARY

The U.S. Department of Energy and EPRI have co-funded this project to improve the control of mercury emissions from coal-fired power plants equipped with wet flue gas desulfurization (FGD) systems. The project has investigated catalytic oxidation of vapor-phase elemental mercury to a form that is more effectively captured in wet FGD systems. If successfully developed, the process could be applicable to over 90,000 MW of utility generating capacity with existing FGD systems and to future FGD installations.

Field tests were conducted to determine whether candidate catalyst materials remain active towards mercury oxidation after extended flue gas exposure. Catalyst life will have a large impact on the cost effectiveness of this potential process. A small catalyst test unit was used to test the activity of four different catalyst materials for a period of up to six months at each of three utility sites. The catalyst materials were tested in the form of powders dispersed in fixed sand beds. Catalyst testing was completed at the first site, which fires Texas lignite, in December 1998 and at the second test site, which fires a Powder River Basin subbituminous coal, in the fall of 1999. Testing at the third site, which fires a medium- to high-sulfur bituminous coal, was completed at the end of January 2001.

Tests conducted at the three sites have shown that there are a number of materials that retain high activity towards elemental mercury oxidation over the periods tested, up to six months. Depending on the site, these active materials include metals, carbons, and fly ashes. No one material remained active over the test duration at all three sites, but this comparison is confounded by extraordinary events such as a low temperature excursion that may have adversely affected catalyst activity in the long-term test at Site 1.

The project did not include fundamental research to determine mercury oxidation mechanisms on the catalyst surfaces. However, the differences in performance of catalyst materials between the three sites appear to be due to variations in flue gas conditions. Laboratory testing suggests that flue gas species such as SO_2, SO_3, HCl and NO_X may impact catalyst oxidation activity and/or deactivation rates. The laboratory studies also suggest that trace species such as selenium in the flue gas may play a role in catalyst deactivation.

Laboratory results also indicate that the activities of sand bed materials are, in general, readily restored by regeneration with nitrogen or CO_2 at temperatures up to 700^oF. Sulfur and selenium are the primary species that desorb from the catalysts on regeneration, but it is not certain that catalyst activity is tied to the presence or absence of these species on catalyst surfaces. It is also undetermined as to how long the regenerated materials will remain active relative to the activity of virgin materials.

The sand bed reactor field results appear to successfully predict activity in commercially available catalyst forms. Sand bed reactor results were used to select a palladium-based material for testing in pellet and/or honeycomb forms at Sites 2 and 3, and high activities were also measured for those catalyst forms. Short-term commercial catalyst form tests showed that for the palladium-based material, high elemental mercury oxidation percentages (70% and greater) could be achieved at area velocity values much higher than in typical flue gas SCR applications. The combination of substantially higher area velocities, tighter honeycomb pitch, and lower gas temperatures (300 vs. 700°F [149 vs 371°C]) suggest that a catalytic mercury oxidation reactor could be substantially smaller than a typical SCR application (e.g., less than 1/10th the size of an SCR reactor).

Preliminary process cost estimates indicate that a catalytic mercury oxidation process could be a less expensive approach for achieving 80 to 90% overall mercury control by plants equipped with FGD than employing carbon injection, which is perceived to be the most commercially available mercury control technology. These estimates are based on a palladium-based catalyst, an assumed three-year catalyst life, and catalyst replacement at the end of each three-year period. The ability to use lower cost (than palladium) catalyst materials, longer catalyst life than three years, and/or the ability to regenerate rather than replace catalysts could improve on the economics of this process.

Flue gas characterization efforts conducted as part of this project have shown that flue gas mercury concentrations can vary widely at a given power plant, in most cases due to variations in coal sources and/or fuel quality variations within a single mine. This variability underlines an advantage of a catalyst-based system for enhancing mercury removal by FGD systems: the ability to achieve high removal efficiencies is relatively insensitive to mercury concentrations in the flue gas. In contrast, carbon injection technology requires monitoring of mercury concentrations to ensure optimum performance. Injecting at too low a rate for the current flue gas mercury concentration could lead to poor removal, while injecting at too high a rate will result in poor carbon utilization.

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INTRODUCTION

The 1990 Clean Air Act Amendments mandated the U.S. Environmental Protection Agency (EPA) to study the health effects caused by hazardous air pollutants (HAPs) from electric utility plants, including a separate study of the effect of mercury emissions. Most HAPs of concern in power plants occur in the particulate phase and are therefore removed in particulate control devices. However, mercury, although present in extremely low concentrations, primarily occurs in the vapor phase. Therefore, particulate removal devices are generally not effective at removing mercury from flue gas and alternative removal methods are needed.

In 1999, EPA instituted a mercury Information Collection Request (ICR), whereby all coal-fired electric utility plants in the U.S. were required to measure and report mercury and other species concentrations in a representative sampling of the coal fired. As part of that ICR, a number of units were required to conduct flue gas sampling for speciated mercury concentrations upstream and downstream of the last emissions control device in their flue gas path. Late in 2000, EPA announced that they would promulgate mercury control regulations for coal-fired power plants, although the form of those regulations is not yet known.

A number of previous research programs have studied mercury emissions from power plants and methods for reducing these emissions. The U.S. Department of Energy's National Energy Technology Laboratory (DOE/NETL) has funded the project discussed in this report to investigate a process for improving the ability of existing wet FGD systems to control mercury emissions from coal-fired power plants. The project was conducted under a cost-sharing PRDA agreement between DOE/NETL, EPRI, and URS Corporation (formerly Radian International LLC).

The proposed process would use a catalyst material to oxidize vapor-phase elemental mercury. Vapor-phase mercury generally exists in two forms in utility flue gas—as elemental mercury and as water soluble, oxidized mercury (the predominant form is believed to be $HgCl_2$). Previous results have shown that wet scrubbers effectively remove oxidized mercury from the gas but are ineffective at removing elemental mercury. Since elemental mercury is present in most flue gas streams and is the predominant form in some, this process can potentially improve overall mercury removal in wet scrubbers by converting the elemental mercury to a form that is more readily scrubbed.

This project was conducted in two phases. During Phase I, several catalyst materials were identified in the laboratory as being able to oxidize elemental mercury. This ability was confirmed in pilot-scale tests and in short-term, slipstream field tests. Pilot tests also confirmed the removal of catalytically oxidized mercury across a wet FGD system. A separate Phase I report was issued in August 1998.[1]

Phase II began in April 1998, and has investigated catalyst life by exposing active catalyst materials to flue gas for an extended period of time at each of three coal-fired power plants. The objective of this testing was to predict required catalyst quantities and catalyst life for future full-scale application of the technology. Results from each of the three sites have been detailed in Topical Reports[2,3,4]. Also, several papers have been presented detailing results from this project[5,6,7]. This Final Report provides a summary and discussion of results for each of the three sites, but the reader is referred to the Topical Reports and/or technical papers for details of the testing conducted at each site.

Section 2 of this report describes the technical approach for Phase II and Section 3 presents Phase II field test results. In Section 4, the results of related laboratory testing are presented, and Section 5 discusses preliminary economics for the catalytic process under development. A summary of the project results is made in Section 6, and a brief acknowledgement is made in Section 7.

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PHASE II TECHNICAL APPROACH

Based on promising Phase I results, DOE/NETL funded a Phase II effort, which included the following objectives:

- Evaluate the ability of catalyst materials to oxidize elemental mercury at three full-scale, coal-fired utility sites;

- Estimate the life of these catalyst materials in three different flue gas streams; and

- Estimate the amount of catalyst required to achieve at least 70% oxidation of the elemental mercury in these flue gas streams.

Phase II testing addressed two critical issues – the life of the catalysts (i.e., how long will the catalysts oxidize mercury?) and the applicability of the process for the U.S. electric utility industry (i.e., are there coals/plants for which the catalysts work more or less effectively?). These issues were addressed by conducting long-term catalyst tests at three full-scale utility sites. Catalyst oxidation efficiency and life will ultimately affect the design of any subsequent commercial process and its economics. Also included in Phase II were field tests of "advanced" or commercial catalyst forms and laboratory related laboratory testing. Each form of testing is described below.

Field Test Program

Figure 2-1 illustrates the catalyst test unit, which was designed to expose catalyst materials to a slipstream of flue gas from a coal-fired boiler for an extended period. The test unit consisted of a heated box that was mounted directly to a flue gas duct, and was small enough to be moved from site to site. Flue gas was continuously drawn from the duct through a heated glass probe and passed through a quartz filter before contacting the catalyst beds. Although in future full-scale systems, the catalyst would be exposed to fly ash remaining in the flue gas downstream of the particulate control device, residual fly ash was removed in the test unit to prevent plugging of the sand beds. A commercial catalyst configuration (e.g., a honeycomb) would be designed to avoid plugging with ash.

After the filter, the flue gas flowed through three parallel catalyst test cells. Each test cell contained two packed beds of catalyst material. Figure 2-2 illustrates the arrangement of the catalyst beds. Catalyst bed temperatures were controlled by adjusting temperatures in the heated box. The gas flow rate through each test cell was continuously monitored, and gas flow rates were periodically adjusted with manual valves. After flowing through the cells, the flue gas passed through a condenser to remove moisture then to sample pumps. At the normal flue gas flow rate, the superficial gas velocity through a test cell was about 18 ft/min (0.1 m/s), which
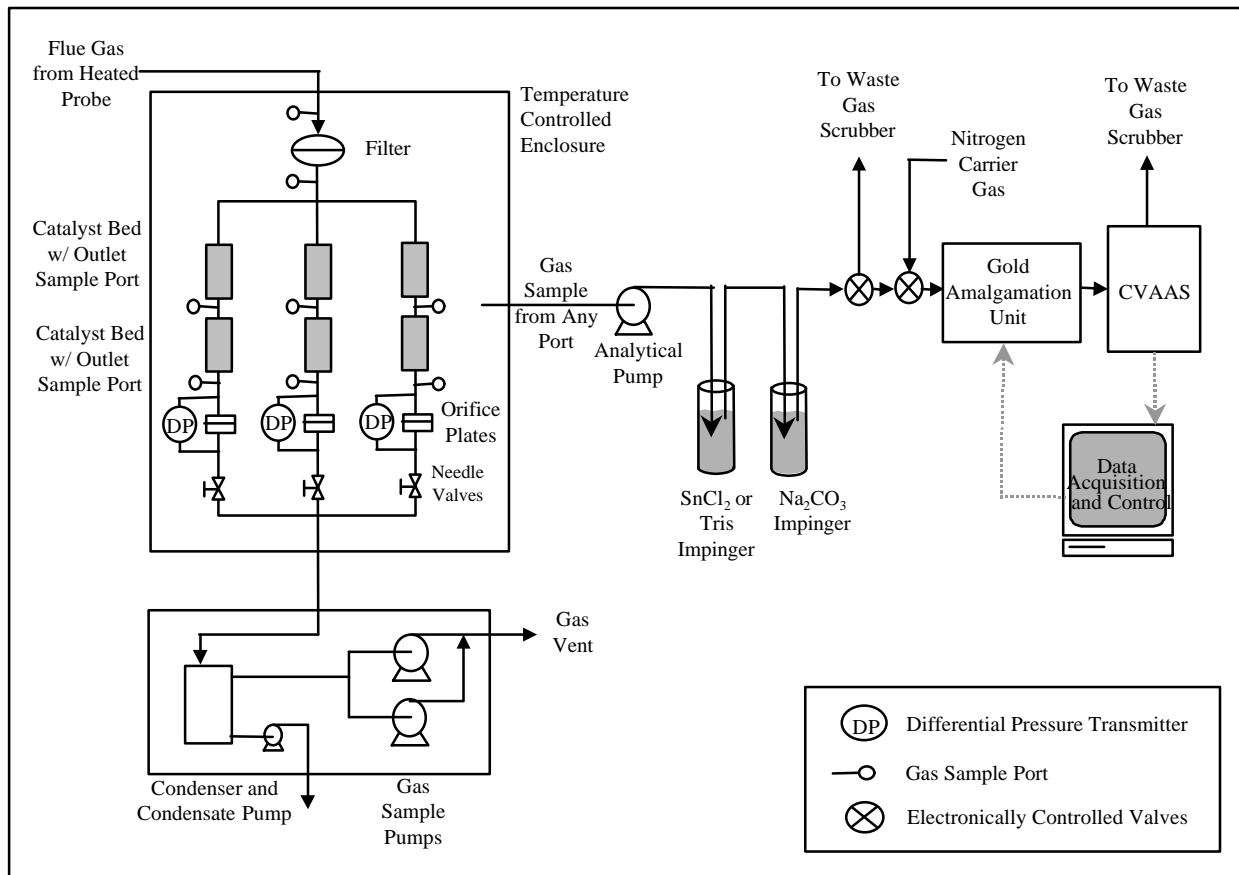
Figure 2-1
Schematic of Field Test Unit and Semi-continuous Mercury Analyzer
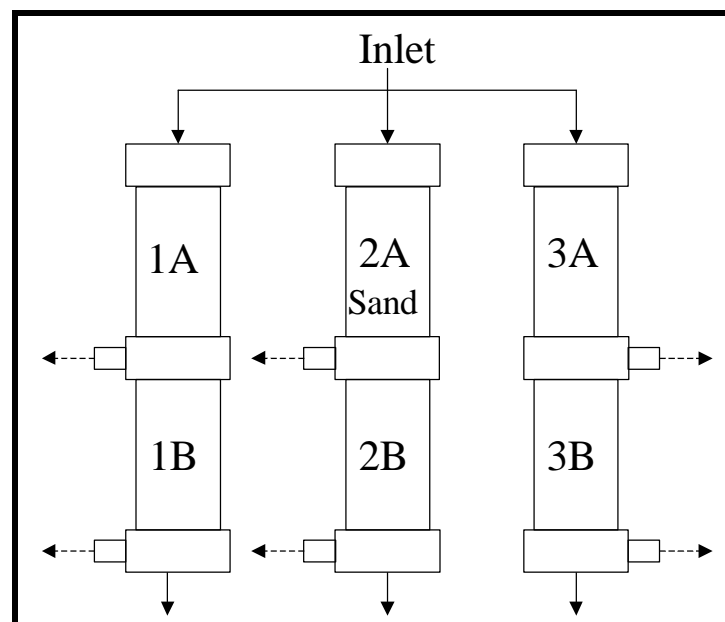
Figure 2-2
Catalyst Holder Arrangement in the Field Test Unit

is similar to the gas velocity through a fabric filter in the EPRI COHPAC configuration (i.e., a high-ratio pulse-jet fabric filter installed downstream of an ESP).

There were two catalyst beds in series in each of the three test cells, so up to six different catalyst materials could potentially be tested simultaneously. However, one bed typically contained a sand bed "blank," and another cell typically had two beds containing the same catalyst material in series, to provide oxidation data at two space velocities (i.e., different ratios of gas flow rate to catalyst volume). Consequently, only four different catalyst materials were typically tested at once.

The catalyst materials in the test cells were diluted with sand. The sand improved gas flow distribution by providing a thicker bed and greater gas pressure drop. Test ports were located at the outlet of each catalyst bed and at the inlet and outlet of the quartz filter. Mercury samples could be collected upstream and downstream of all catalyst beds. By measuring the change in elemental mercury concentration across each bed, the mercury oxidation across each could be determined.

Mercury measurements were made using a semi-continuous mercury analyzer developed for EPRI. As shown in Figure 2-1, flue gas was pulled from the catalyst test unit at about 1 L/min through a Teflon[®]-lined pump and passed through a series of impingers. To measure total mercury in the flue gas, the impinger solutions contained stannous chloride ($SnCl_2$) followed by a sodium carbonate (Na_2CO_3) buffer. The $SnCl_2$ solution reduces all flue gas mercury species to elemental mercury. The Na_2CO_3 solution removes acid gases, thus protecting the downstream, analytical gold surface. Gas exiting the impingers flowed through a gold amalgamation column where mercury in the gas was adsorbed. After concentrating mercury onto the gold for a fixed period of time (typically 10 minutes), the mercury was thermally desorbed (>700°C) from the column into a nitrogen purge stream that flows to a cold-vapor atomic absorption spectrophotometer (CVAAS) for analysis. The flue gas total mercury concentration was measured semi-continuously with a 10-minute sample time followed by a 10-minute analysis period.

To measure elemental mercury in the flue gas, the $SnCl_2$ impinger was replaced with one containing tris(hydroxymethyl)aminomethane (Tris) solution. The Tris solution has been shown to capture oxidized mercury while allowing elemental mercury to pass through without being altered[1]. Mercury passing through the Tris solution was analyzed as described above and assumed to represent the elemental mercury content in the gas sampled. The difference between the total mercury concentration (stannous chloride impinger train) and elemental mercury concentration (Tris impinger train) was taken as the oxidized mercury concentration. The analyzer was calibrated versus elemental mercury vapor standards and results were confirmed at each site by performing manual sampling by the draft Ontario Hydro method. The Ontario Hydro method for determining the mercury speciation involves analyzing the oxidized and elemental mercury captured in an impinger train containing solutions of potassium chloride (KCl), potassium permanganate ($KMnO_4$), and peroxide (H_2O_2). In most cases, the analyzer results and the draft Ontario Hydro method results agreed well. However, at the last site, Site 3, the two agreed well at the beginning of the test period, but at the end of the test period, the analyzer showed much lower elemental mercury concentrations in the sample gas than was measured by

the Ontario Hydro method in the flue gas. The reason for this discrepancy was never successfully determined.

The most promising catalyst materials were tested for up to six months at each of three utility power plants. At each site, an initial set of short-term screening tests was conducted to determine the most active catalysts for that site and to allow comparing the performance of several catalyst materials from site to site. Each screening test was run for two to four days, or in some cases up to two weeks, to allow the catalysts to approach mercury adsorption equilibrium before measuring oxidation performance. Based on the screening test results, four catalyst materials were selected for continuous long-term (five- to six-months) flue gas testing at each site. Periodic performance measurements were taken to determine if oxidation changed with time. Between performance measurements, the test unit operating conditions were monitored remotely using mobile communications. This approach was used to measure catalyst life for four catalyst materials at each of the three coal-fired facilities. The four materials were not all the same from site to site, although some materials were tested at all three sites.

The test sites were chosen to provide a range of flue gas compositions and correspond with the three solid fossil fuels used for power generation in the U.S.: bituminous coal, subbituminous coal, and lignite. Of the installed FGD capacity in the U.S., about 48% (on a megawatt basis) is on power plants that fire bituminous coal, 40% on plants that fire subbituminous coal, and 12% on plants that fire lignite. The first test site fires a medium-sulfur Texas lignite, the second site fires a low-sulfur Powder River Basin subbituminous coal, and the third fires a medium- to high-sulfur bituminous coal.

Commercial Catalyst Form Tests

During the long-term testing of catalyst sand beds at Sites 2 and 3, additional tests were conducted to evaluate the activity of a catalyst material in a commercially available form. Two commercial catalyst forms were tested at Site 2, with the catalyst material wash coated either onto extruded alumina pellets or onto an alumina honeycomb support such as is used in flue gas NO_X selective catalytic reduction (SCR). At Site 3, only the honeycomb configuration was tested.

These tests were conducted in an apparatus operated in parallel with the long-term field test unit described above. The honeycomb catalyst test apparatus drew flue gas from a quartz-lined probe installed in a port next to that of the long-term field test unit. Flue gas was drawn through heated Teflon® sample lines to one or more Teflon® catalyst holders placed in a temperature-controlled, heated box. From the catalyst holder(s), the treated flue gas was pulled through a vacuum pump that discharged the small amount of flue gas to the atmosphere. Flue gas flow rates were measured with a calibrated rotameter on a periodic basis. Mercury concentrations were measured upstream and downstream of each catalyst holder using the field analytical instrument described above. These analyses were conducted when the analyzer was not being used to measure mercury concentrations for the long-term field test unit.

The catalyst holders contained either 5-mm-diameter extruded beads of catalyst material on alumina, or 5/8-inch (16-mm) diameter "cores" of catalyst material wash coated on a honeycomb

alumina support. These catalyst forms were tested over relatively short time periods (i.e., days or weeks rather than months), as the primary objective of these tests was to measure activity in this configuration rather than catalyst life.

The testing was focused on flue gas flow rates that would correspond with commercially viable catalyst reactor sizes. If we assume that mercury oxidation occurs primarily on the external surfaces of the catalyst materials (i.e., not in the pores), a design term called area velocity probably represents the best parameter for scaling small-scale reactor results to a commercial catalyst bed design. Area velocity is calculated as the flue gas flow rate at standard conditions divided by the catalyst material's geometric (external) surface area. SCR catalysts typically operate at area velocities ranging from 15 to 30 standard ft/hr (4.3 to 8.7 Nm/hr). If mercury catalysts can be proven effective at similar or higher area velocities, it is likely that honeycomb support structures could be utilized in a reactor of a commercially viable size. The actual area velocities tested for mercury catalysts at Site 2 ranged from 110 to 860 standard ft/hr (32 to 250 Nm/hr) for the bead catalyst form, and from approximately 105 to 240 standard ft/hr (30 to 69 Nm/hr)for the honeycomb. At Site 3, the actual area velocities tested for honeycomb catalysts ranged from approximately 90 to 170 standard ft/hr (26 to 49 Nm/hr).

Laboratory Tests

Laboratory tests were also conducted to support the field tests. Typically, a simulated flue gas containing elemental mercury flowed across a fixed-bed reactor containing catalyst material. The gas exiting the bed was analyzed semi-continuously by the technique described above to determine the fraction of inlet elemental mercury oxidized across the bed. Mercury speciation across the catalyst bed was determined after adsorption equilibrium had been established.

The simulated flue gas was prepared from reagent gases using calibrated flow meters. Elemental mercury was added by passing nitrogen carrier gas across a diffusion cell that contained an elemental mercury permeation tube. The amount of diffused mercury was controlled with the flow of nitrogen and the temperature of the diffusion cell. The mercury-containing nitrogen was then mixed with other flue gas components (SO_2, HCl, NO_X, O_2, CO_2, and H_2O) at constant temperature before the gas entered the reactor.

The fixed-bed reactor was a temperature-controlled, vertical Pyrex column that contained a mixture of the catalyst material and sand. The gas rate was typically about 1.4 L/min at 300°F (149°C), which resulted in a superficial gas velocity through the bed of about 30 ft/min (0.15 m/s).

The bench-scale unit was used to simulate flue gas conditions at each full-scale test site prior to testing in the field, to obtain information about the expected effects of flue gas composition on oxidation. The bench-scale unit was also used to investigate the regeneration of spent catalysts. Spent catalysts were regenerated by exposure to various atmospheres at elevated temperatures, then tested for mercury oxidation activity in simulated flue gas. Other tests were run on the bench-scale unit in an effort to develop a better understanding of mercury oxidation and catalyst deactivation mechanisms.

References

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FIELD TESTING RESULTS

This section describes the results of field testing conducted at the three sites included in this project. First, this section includes a description of each site and some discussion about the site selection process. Results are then presented from short-term mercury oxidation catalyst screening tests at each of the three sites, followed by the results of longer-term catalyst activity tests. Both the short-term and longer-term tests used sand-bed reactors as described in Section 2. For Sites 2 and 3, results are also presented for short-term tests conducted with commercially available catalyst configurations. Finally, results are presented from flue gas, coal, and fly ash characterization efforts conducted as part of the test programs at each site.

Site Descriptions

Site 1

Site 1 is a large (>500 MW) wall-fired unit that fires Texas lignite. It has an ESP for particulate control and a wet limestone FGD system. It was selected as the first site because of the results of prior testing at that site as part of Phase I of this project. Based on those results, it was known that Site 1 has a relatively high concentration of elemental mercury in the flue gas downstream of the ESP (FGD inlet location). Also, the Phase I results suggested that several candidate catalyst materials would show high activity towards elemental mercury oxidation in the Site 1 flue gas.

Table 3-1 summarizes the flue gas conditions measured at Site 1 during this project. As expected, the elemental mercury concentrations in the flue gas were relatively high, ranging from approximately 4 to 20 $\mu g/Nm^3$ over the course of testing. The flue gas SO_2 concentrations of 1000 to 1500 ppm were consistent with what would be considered a medium-sulfur Texas lignite. Also, because of the alkaline ash associated with this lignite, the flue gas SO_3 and HCl concentrations at the ESP outlet/FGD inlet location were relatively low, each less than 2 ppm.

Site 2

Site 2 is a moderately large (400-600 MW) tangentially-fired unit that fires a blend of Wyoming, Powder River Basin subbituminous coals. It has an ESP for particulate control and a wet limestone FGD system. Site 2 was selected because Wyoming coal is fired by the greatest number of megawatts of generating capacity among FGD-equipped power plants that fire subbituminous coal.

Table 3-1
Measured FGD Inlet Flue Gas Conditions at Site 1

Parameter	Phase II – December 1998	Phase II – May 1998	1997 Phase I
Inlet $[Hg^0]$*	21 µg/Nm^3	4.2 µg/Nm^3	10 µg/Nm^3
Inlet [Hg total]*	31 µg/Nm^3	17 µg/Nm^3	13 µg/Nm^3
Hg % Oxidation	33%	76%	22%
Average SO_2 (wet basis)	1000 ppm	1500 ppm	1400 ppm
SO_3 (dry basis)	-	0.7 ppm	-
HCl (dry basis)	-	1.8 ppm	1 ppm
Average NO_X (wet basis)	140 ppm	150 ppm	190 ppm

*By Method 29T in May 1998, Ontario Hydro (KCl) method in December 1998. Phase I results are for the semi-continuous mercury analyzer

Table 3-2 summarizes the flue gas composition at Site 2. Flue gas mercury concentration measurements were first made at Site 2 late in 1998, using the draft Ontario Hydro method. The results showed an average total mercury concentration of 12.0 µg Hg/Nm^3 and an average gas phase elemental mercury concentration of 8.8 µg Hg/Nm^3 in the flue gas upstream of the FGD system, corresponding with an average mercury oxidation percentage of 27%. These results confirmed that the flue gas at this site has an adequate elemental mercury concentration to support mercury oxidation catalyst testing.

Table 3-2
Measured FGD Inlet Flue Gas Conditions at Site 2

Flue Gas Parameter	Site 2 Measured Value
FGD Inlet $[Hg^0]$, by Ontario Hydro Method	8.8 µg/Nm^3
FGD Inlet [Hg total], by Ontario Hydro Method	12.0 µg/Nm^3
Hg % Oxidation	27%
SO_2	300 ppm (wet basis)
SO_3	<0.2 ppm (dry basis)
HCl	1.1 ppm (dry basis)
Cl_2	1.2 ppm (dry basis)
NO_X	160 ppm (wet basis)

Other flue gas analyses were conducted in 1999. These results are also shown in Table 3-2. The results showed that the HCl and Cl_2 concentrations at Site 2 were, as expected, quite low (about

1 ppm each). SO_3 concentrations were measured at the FGD inlet location by the Controlled Condensation System (CCS) method, and showed very low values as would be expected for Powder River Basin coal fired in a tangentially-fired boiler. Finally, Table 3-2 includes typical FGD inlet SO_2 and NO_X concentrations as measured by the Site 2 CEM system, which are consistent with a Powder River Basin coal fired in a boiler equipped with low NO_X burners.

Site 3

Site 3 is a large (>750 MW) tangentially-fired unit that fires a blend of Pennsylvania and West Virginia bituminous coals, with an average sulfur content of about 2.6 wt %. It has an ESP for particulate control. An ammonia-injection conditioning system installed in the flue gas path between the air heater and ESP is used to improve ESP performance. SO_2 (and HCl) emissions are controlled with a limestone reagent wet FGD system designed for 95% SO_2 removal. All of the flue gas from Site 3 is scrubbed; there is no gas bypass.

Table 3-3 summarizes the flue gas conditions measured at Site 3 during this project. The Site 3 flue gas contained higher concentrations of SO_2, SO_3 and HCl than the first two sites, but lower elemental mercury concentrations.

Table 3-3
Measured FGD Inlet Flue Gas Conditions at Site 3

Flue Gas Parameter	Site 3 Measured Value
FGD Inlet [Hg^0], by Ontario Hydro Method	3-4 μg/Nm^3
FGD Inlet [Hg total], by Ontario Hydro Method	8-13 μg/Nm^3
Hg % Oxidation	58-74%
SO_2	1530-1740 ppm (wet basis)
SO_3	2.8-5.6 ppm (dry basis)
HCl	79 ppm (dry basis)
Cl_2	0.7 ppm (dry basis)
NO_X	Not Measured

A bituminous coal plant was selected to host Site 3 because bituminous coal is fired by the greatest number of megawatts of generating capacity among FGD-equipped power plants. However, as described below, there was some difficulty in identifying a bituminous coal site that was known to have adequate elemental mercury concentrations in the flue gas to support quantitative mercury oxidation catalyst performance testing.

In EPA's mercury ICR program, most bituminous coals were measured to contain about 0.1 ppm (by weight) of mercury, which typically corresponds with about 10 μg/Nm^3 of total mercury in the boiler exit flue gas. Most bituminous coals were observed to produce a flue gas with a highly

oxidized mercury content, typically on the order of 70 to 80% oxidized or greater. Such coals produce a flue gas with about 2 $\mu g/Nm^3$ of elemental mercury or less. At such low elemental mercury concentrations, it is difficult to measure the effectiveness of mercury oxidation catalysts. It would be desirable to identify catalysts capable of achieving at least 90% oxidation of elemental mercury in flue gas. For a flue gas with only 2 $\mu g/Nm^3$ of elemental mercury, 90% oxidation would leave only 0.2 $\mu g/Nm^3$ of elemental mercury, which is at or below the detection limit for the field mercury analyzer being used to evaluate catalyst performance in this project.

Note that a catalytic oxidation process may be applicable to bituminous coal fired units even with total mercury concentrations of 10 $\mu g/Nm^3$, and 2 $\mu g/Nm^3$ or less of elemental mercury. It will depend on how future mercury control regulations are written as to what level of mercury oxidation might be required such that mercury removal by a wet FGD system would be adequate to achieve compliance. Some plants with naturally occurring mercury oxidation percentages of 70 to 80% or greater may require further oxidation to ensure compliance. However, as described above, such sites are not ideal for testing and quantifying catalyst performance because of the low elemental mercury concentrations that result downstream of an effective catalyst.

In the EPA ICR data, a number of coals from Ohio and Pennsylvania were reported to contain, on average, much higher concentrations of 0.2 to 0.3 ppm of mercury or greater. The flue gases from firing these coals were expected to contain 20 $\mu g/Nm^3$ to 30 $\mu g/Nm^3$ of total mercury. Even with 80% mercury oxidation, these flue gases should contain approximately 4 to 6 $\mu g/Nm^3$ of elemental mercury, which would be within the desired range for Site 3 catalyst testing.

The host for Site 3 fires a blend of coals, including some Pennsylvania coals that contain a higher mercury content. The average mercury content of the coal fired at Site 3 was reported at 0.25 ppm during the ICR program. However, during the initial site visit the flue gas mercury concentrations at the Site 3 FGD inlet location, as determined by the EPRI semi-continuous flue gas mercury analyzer describe in Section 2, were lower than expected. Total mercury concentrations in the FGD inlet flue gas were measured to range from 6 to 16 $\mu g/Nm^3$, and elemental mercury concentrations ranged from 3 to nearly 7 $\mu g/Nm^3$. Mercury oxidation percentages averaged 62 to 70%. Manual flue gas sampling by the draft Ontario Hydro method was conducted a few weeks later, and verified the field analyzer results (see Table 3-3). However, although lower than expected, the measured elemental mercury concentrations were judged to be adequate to support continued catalyst testing at this site.

Several potential reasons were identified as to why the flue gas mercury concentrations were lower than expected. The most probable explanation is that the Site 3 boiler is equipped with "low NO_X" burners, which typically result in relatively high LOI levels in the fly ash produced. Based on previous results from Sites 1 and 2 with Subbituminous Ash #5 as a catalyst material, it was speculated that the ash at Site 3 adsorbs and/or oxidizes a portion of the flue gas mercury. This adsorption lowers the flue gas mercury concentration at the ESP outlet/FGD inlet location relative to the amount of mercury in the coal. Data collected later in the Site 3 test period indicated this to be the primary reason why lower than expected mercury concentrations were measured in the FGD inlet flue gas at Site 3. These data are presented and discussed later in this section.

Short-term Catalyst Screening Test Results

Site 1 Short-term Results

In May 1998, a series of short-term catalyst screening tests were conducted at Site 1. Based on lab results at simulated Site 1 conditions (see Section 4), it was decided to field test a number of commercial and experimental activated carbons, two palladium-based catalysts and four fly ashes. The four fly ashes included: Subbituminous Ash #5, Bituminois Ash #3, Bituminous Ash #2b, and Subbituminous Ash #4. Iron-based catalysts were not tested at Site 1 due to their poor performance on the simulated Site 1 flue gas.

Table 3-4 summarizes the catalyst materials tested and results from the Site 1 catalyst screening tests. The indicated mass was mixed with sand to produce a 75 g bed and the mixture was placed in one of six test cells. Some catalysts were placed in two packed beds in series while others were tested using only one bed. Catalyst materials with more than one mass reported in Table 3-4 were tested as two beds in series. For all tests, the catalyst operating temperature was 300^oF (149^oC), and the flue gas flow rate through the bed was 5 l/min (measured downstream of the beds at 85^oF [29^oC]).

During these short-term tests, two field sand blank measurements were made which resulted in an average oxidation of 5.8%. This indicates that the sand mixed with each catalyst material did not significantly affect the measured mercury oxidation results. Note that the oxidation percentages shown in this table and throughout this report are calculated from the decrease in elemental mercury across the beds, and do not just represent the total mercury oxidation percentage in the flue gas at the bed outlet. The latter would generally be a higher percentage because a portion of the total mercury content in the gas is already oxidized before entering the catalyst test unit. The percentages shown also account for mercury oxidation measured across the sand blank, to account for any contribution to elemental mercury oxidation by the sand content in each bed.

The total mercury concentrations at the inlet and outlet of the catalyst beds were nearly equal during most tests, indicating that most of the catalyst materials had reached or were near an equilibrium where they were no longer adsorbing mercury from the flue gas. The exceptions were when testing catalyst materials Carbon #6, Subbituminous Ash #4, and Pd #1. The lower outlet mercury concentrations measured during these tests most likely indicate that mercury was being adsorbed by the catalyst materials when the measurements were taken.

All of the carbon-based catalysts achieved greater than 90% elemental mercury oxidation at Site 1 with the exception of Carbon #5. This material showed high oxidation percentages in the lab but not in the field. The palladium-based catalysts also showed reasonably high oxidation percentages, but their performance was lower than that of the carbon-based materials. The fly ash samples were mostly limited to about 60% oxidation, with the exception of Subbituminous Ash #5, which has a very high loss on ignition. These data suggest that the unburned carbon content in Subbituminous Ash #5 affects mercury oxidation, since its performance was similar to that of the carbon-based materials (although it was tested at a much higher catalyst loading).

Table 3-4
Results of Short-term Catalyst Performance Screening Tests at Site 1

Sample ID	Sample Loading (mg catalyst)	Mercury Adsorption Breakthrough (% of inlet Hg)	Elemental Mercury Oxidation (% of inlet Hg^0)
Carbon-based Catalyst Materials			
Carbon #1 – First Bed	75	-	100
Carbon #1 – Both Beds	150	100	100
Carbon #2 – First Bed	75	-	100
Carbon #2 – Both Beds	150	100	97
Carbon #3 (One Bed)	75	100	93
Carbon #4 – First Bed	75	-	93
Carbon #4 – Both Beds	150	93	95
Carbon #5 – First Bed	75	-	53
Carbon #5 – Both Beds	150	90	62
Carbon #6 – First Bed	75	-	97
Carbon #6 – Both Beds	150	81	99
Fly-ash-based Catalyst Materials			
Bituminous Ash #2b (One Bed)	3750	88	56
Bituminous Ash #3 – First Bed	750	-	59
Bituminous Ash #3 – Both Beds	1500	100	61
Subbituminous Ash #4 (One Bed)	3750	75	59
Subbituminous Ash #5 – First Bed	750	-	100
Subbituminous Ash #5 – Both Beds	1500	100	100
Metal-based Catalyst Materials			
Pd #1 – First Bed	750	-	76
Pd #1 – Both Beds	1500	77	90
Pd #3 (One Bed)	750	100	87

Site 2 Short-term Results

During March 1999, the field test unit was installed at Site 2 and short-term screening tests were conducted to evaluate catalyst performance. Six carbon-based catalysts, one fly-ash-based catalyst, and four metal-based catalysts were screened for mercury oxidation activity in the Site 2 flue gas in short-term (three- to nine-day) tests. The catalysts screened for activity in the field were selected on the basis of laboratory tests using simulated Site 2 flue gas. Table 3-5 summarizes the results of the screening tests conducted at Site 2.

For catalysts where results for two beds are listed, the first result is for the upstream bed, and the second result is for the two beds in series. For catalysts for which only one bed is noted, this catalyst was configured in the "2B" cell position (Figure 2-2), downstream of the sand bed "blank." The results for all catalysts have been corrected to account for any observed adsorption or oxidation across the sand bed blank.

The results in Table 3-5 show that only five of the eleven samples achieved elemental mercury oxidation percentages near or above 90%. Three of these five samples were palladium-based catalysts. The Pd #1 catalyst is commercially available, but the Pd #2 and Pd #3 catalysts tested were chemical reagents in powder form. The relative lifetime before deactivation of these three catalysts is not known. However, because it is commercially available as a catalyst, Pd #1 was the only palladium-based catalysts selected for the long-term test at Site 2.

The two carbon-based catalysts that achieved high oxidation, Carbon #4 and Carbon #5, demonstrated substantially lower oxidation in the first bed relative to that with both beds. This either indicates inconsistent mercury measurements for the outlets of the first beds compared to the second bed measurements, or indicates rapid loss of activity of the material in the first beds. The latter would suggest that neither would be a good choice for long-term testing.

Because of the inconsistencies noted in the short-term test results for the carbon materials, an intermediate-length test was conducted with three of the carbon-based catalysts. As mentioned previously, the short-term catalyst screening tests described above were conducted in March 1999. The Site 2 boiler had a scheduled outage coming up in late April, so it was decided to wait to start the long-term test until after the outage. The intermediate-length test with three carbons was conducted in April prior to the outage. Results from this test are summarized in Figure 3-1.

The longer test period (3 weeks) was intended to discern which of three carbon catalysts tested would remain most active, and might therefore be most likely to maintain mercury oxidation activity over the duration of the subsequent long-term test. Carbon #5 showed poor activity/life relative to the other carbons and continually lost activity throughout the test. Carbon #1 and Carbon #6 both exhibited high initial oxidation followed by some degree of deactivation. Carbon #1 lost activity more readily than Carbon #6, indicating that the latter would be a better choice in the Site 2 long-term tests.

Table 3-5
Results of Short-term Catalyst Performance Screening Tests at Site 2

Sample ID	Sample Loading (mg catalyst)	Mercury Adsorption Breakthrough (% of inlet Hg)	Elemental Mercury Oxidation (% of inlet Hg0)
Carbon-based Catalyst Materials			
Carbon #1 – First Bed	150	95	78
Carbon #1 – Both Beds	300	98	72
Carbon #2 – First Bed	75	84	0
Carbon #2 – Both Beds	150	75	32
Carbon #2 – Repeat (One Bed)	75	95	61
Carbon #3 (One Bed)	150	83	77
Carbon #4 – First Bed	150	84	25
Carbon #4 – Both Beds	300	100	89
Carbon #5 – First Bed	75	76	0
Carbon #5 – Both Beds	150	59	93
Carbon #6 – First Bed	150	79	82
Carbon #6 – Both Beds	300	90	78
Fly-ash-based Catalyst Materials			
Subbituminous Ash #5 (One Bed)	1125	11	80
Metal-based Catalyst Materials			
Fe #1 (One Bed)	3750	87	29
Pd #1 – First Bed	3750	89	90
Pd #1 – Both Beds	7500	82	>90
Pd #2 (One Bed)	500	100	95
Pd #3 – First Bed	3750	100	92
Pd #3 – Both Beds	7500	100	>92
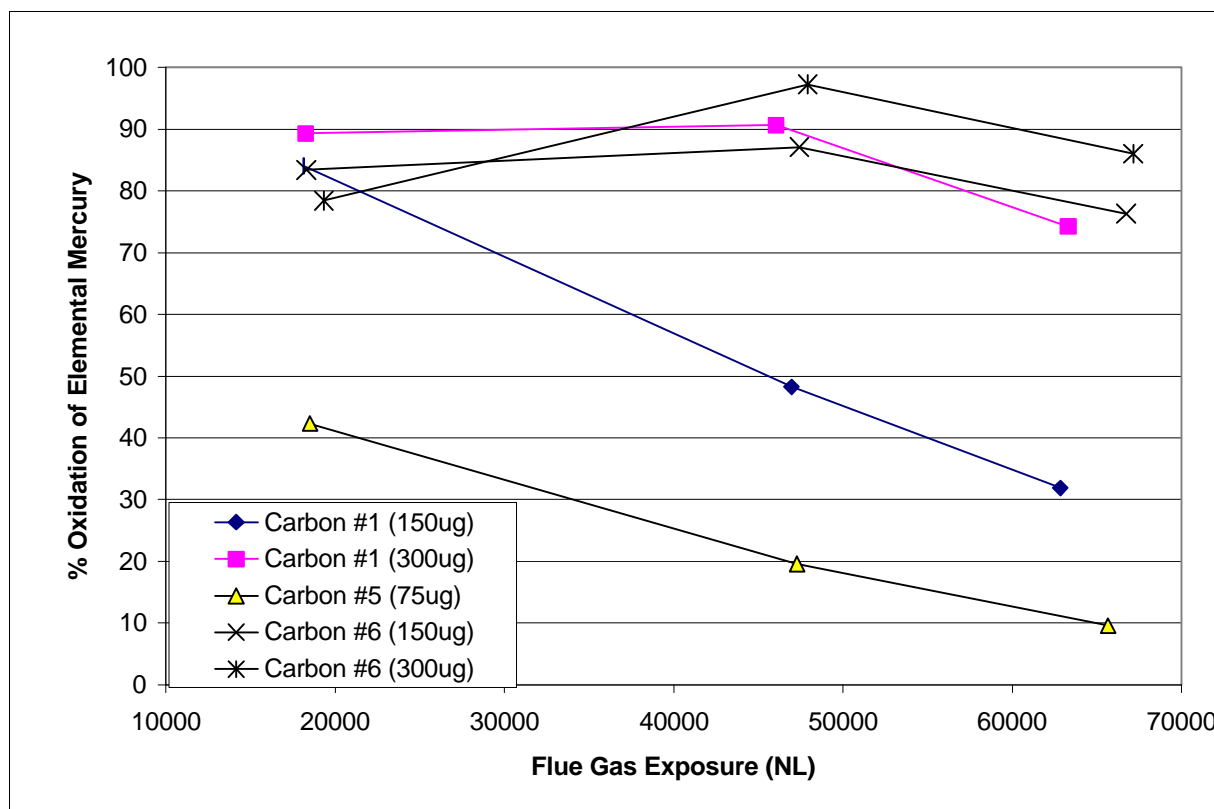
Figure 3-1
Activity of Three Carbon-based Catalysts during a Three-week Exposure to Site 2 Flue Gas

Site 3 Short-term Results

Although the total mercury concentrations were lower than expected at Site 3, the measured elemental mercury concentrations of nominally 3 to 6 μg/Nm^3 were determined to be adequate for mercury oxidation catalyst testing. Based on the results of previous laboratory catalyst screening tests (see Section 4), several catalyst materials were selected for short-term testing at Site 3. Three sets of screening tests were conducted during mid-June through early July 2000. Metal-based catalysts were evaluated in the first screening test set, which went for approximately 5 days, and fly ash materials and Carbon #4 were evaluated in the second screening test set which lasted 7 days. The third screening test set, which included the remainder of the carbon-based catalysts, was run for a longer period of 14 days to ensure that adsorption equuilibrium was reached prior to making mercury oxidation measurements.

The results from the short-term screening tests at Site 3 are summarized in Table 3-6. In general, at the end of the test the metal catalyst materials in the first screening test set were at or near adsorption equilibrium (observed total mercury breakthrough values were near 100%) and the oxidation percentages were high (approximately 90%). Conversely, the ashes and the Carbon #4 in the second set were still adsorbing appreciable amounts of mercury, and the observed oxidation percentages were relatively low (all less than 50%). After a longer, 14-day duration,

Table 3-6
Results of Short-term Catalyst Performance Screening Tests at Site 3

Catalyst Material	Sample Loading (mg catalyst)	Observed Hg Breakthrough (%)	Observed Elemental Hg Oxidation (%)
Carbon-based Catalyst Materials			
Carbon #1 – First Bed	150	86**	73
Carbon #1 – Second Bed	150	20	-
Carbon #2 (One Bed)*	75	63	-
Carbon #4 – First Bed		49	7
Carbon #4 – Second Bed		31	10
Carbon #3 (One Bed)	150	84	93
Carbon #6 (One Bed)	150	68	62
Fly-ash-based Catalyst Materials			
Bituminous Ash #3 (One Bed)*		63	-11
Subbituminous Ash #4 (One Bed)		53	37
Subbituminous Ash #5 (One Bed)	1500	45	44
Metal-based Catalyst Materials			
Fe #1 (One Bed)	3750	87***	90
Fe #5 (One Bed)*		87***	-
Pd #1 – First Bed	3750	94	92
Pd #1 – Second Bed	3750	81	-
SCR (One Bed)		130**	87

* These catalysts were tested downstream of another catalyst, in the "B" catalyst position; if the upstream catalyst showed high activity, little elemental mercury remained at the inlet to the downstream catalyst, so no oxidation percentage could be measured.
** These numbers should be considered approximate due to variability in inlet total Hg concentrations over the course of the day.
*** Total for the two iron-based catalyst beds in series.

the carbons in the third set were approaching adsorption equilibrium and achieved relatively high mercury oxidation efficiencies.

Interpretation of the Site 3 short-term test data in Table 3-6 is confounded by apparent variations in the inlet flue gas total and elemental mercury concentrations during the measurement of

catalyst performance. During a normal test sequence, total mercury concentrations across the test apparatus were evaluated one day, and elemental concentrations during the next day. Inlet concentrations for total and/or elemental mercury were measured at the beginning and end of each test day, and the outlet concentrations from each of the six catalyst holders were measured throughout the day. Either the average or an interpolation between the beginning and end of day values was used as the inlet concentration for the upstream catalysts. For the downstream position catalysts, the outlet of the upstream catalyst was used as the inlet value. This approach works well when inlet concentrations remain relatively stable throughout the day, but makes data interpretation difficult when inlet concentrations vary significantly, as they were observed to do at Site 3.

During the "total mercury" measurements for short-term Test 1 (metals), the total mercury concentrations in the inlet flue gas varied over a wide range, from a morning average of 12.9 $\mu g/Nm^3$ to an evening average of 6.8 $\mu g/Nm^3$. For short-term Test 2 (ashes and Carbon #4), the morning and afternoon average inlet values were 10.0 $\mu g/Nm^3$ and 13.3 $\mu g/Nm^3$, respectively. The inlet elemental mercury concentrations similarly varied throughout each test day, although over a narrower range. During short-term Test 1, inlet elemental mercury concentrations varied from an average of 4.5 $\mu g/Nm^3$ in the morning to 3.0 $\mu g/Nm^3$ in the afternoon. For Test 2, the corresponding averages were 6.1 $\mu g/Nm^3$ in the morning and 4.4 $\mu g/Nm^3$ in the afternoon. These observed variations are most likely caused by fluctuations in the coal blend fired at Site 3. As mentioned above, Site 3 fires a blend of a number of Pennsylvania and West Virginia coals, with widely varying mercury contents reported for each.

The observed variations in inlet total and elemental mercury concentrations no doubt contribute to errors in some of the results reported. For example, in short-term Test 1, the outlet total mercury concentration from the NO_X catalyst bed was higher than the inlet value, resulting in an apparent mercury breakthrough percentage of 130%. However, these errors will not greatly affect results as to which catalyst materials showed the highest oxidation percentages. High oxidation percentages correspond with very low outlet concentrations (less than 1 $\mu g/Nm^3$). The calculated oxidation percentages for high-activity materials are consequently not very sensitive to the measured inlet concentration.

Total mercury concentration variations during the day can adversely affect mercury adsorption measurements, though, since the "inlet" mercury concentration value can vary by a factor of two at Site 3 with time. When the inlet total mercury concentrations were measured for short-term Test 3 (carbons), the concentrations varied from about 12 $\mu g/Nm^3$ late in the morning to 22 $\mu g/Nm^3$ later that afternoon. Thus, in the Test 3 results, the percent mercury breakthrough values for the first bed of Carbon #1 should be considered approximate. For the other beds, the upstream concentrations were measured very close in time to the downstream measurements, so those percent breakthrough values are likely to be more accurate. In general, during short-term Test 3 the upstream carbons were near adsorption equilibrium (>80% mercury breakthrough) while those in the downstream position were still adsorbing appreciable quantities of mercury (20% to 68% mercury breakthrough).

Because of elemental mercury concentration variations in the flue gas during the short-term Test 3 measurements, the oxidation percentages for the carbon-based catalysts should be considered

approximate. Carbon #3 was clearly the most active, but it would be difficult to distinguish between the performance of Carbon #1 and Carbon #6 with these results. It was not possible to measure the performance of Carbon #2, because of the low elemental mercury concentrations remaining in the flue gas downstream of the Carbon #3 bed.

There were a couple of problems noted during these short-term tests. On the final day of the second short-term test, the measured temperature of catalyst train 2 dropped to 190^oF (88^oC) overnight. The reason for this drop was not apparent, and the catalyst train temperature reading was restored to 300^oF (149^oC) for several hours before measuring the outlet elemental mercury concentrations from Subbituminous Ash #5. However, this temperature excursion may have adversely affected the activity of the catalyst material, and may account for the lower than expected activity of Subbituminous Ash #5.

During initial catalyst performance measurements for short-term Test 3, project team members noted a low bias in elemental mercury concentrations measured upstream of the catalyst beds. The bias was traced to a buildup of fly ash in the filter at the flue gas inlet to the catalyst test unit. Apparently the fly ash loading at Site 3 at the FGD inlet location is high enough that over a period of two weeks or longer, a great deal of fly ash can collect on the filter upstream of the catalyst beds. Also, it was apparent from the dark color that the ash has a relatively high LOI, and correspondingly was anticipated to have some adsorption capacity for mercury. The filter was cleaned and the catalysts were placed back in service. The catalyst performance data reported for the carbons tested in short-term Test 3 were collected after the filter was cleaned and the catalysts were put back in service.

Comparison of Screening Test Results from the Three Sites

It is interesting to compare which catalyst materials were most active in the short-term tests at the three sites. Table 3-7 lists the materials that were observed to achieve at least 80% oxidation in short-term tests at each of the three sites. For the carbon-based catalysts, the number of carbons that were active decreased from five at Site 1 to three at Site 2, and only one at Site 3, although the latter results may be confounded by elemental mercury concentration variations during the short-term test measurements. The differences in carbon activity from site to site is assumed to be due to the differing concentrations of other flue gas species, such as SO_2, SO_3, HCl and NO_X. The most active fly ash at the first two sites was Subbituminous Ash #5, but this material was not as active at Site 3. The latter result is possibly confounded by a temperature excursion during short-term Test 2 at Site 3, though. Of the metal-based catalysts, the palladium materials were active at all three sites, while the iron-based catalyst and SCR catalyst were only active in the bituminous coal flue gas environment of Site 3. Note that the latter two were not tested in the field at Sites 1 or 2, but were eliminated based on laboratory results at simulated Site 1 and 2 flue gas conditions.

Table 3-7
Comparison of Most Active Catalyst Materials in Short-term Tests at the Three Sites

Parameter	Site 1	Site 2	Site 3
Coal Type	Texas Lignite	Power River Basin	Bituminous
Carbon-based Catalysts	Carbon #1 Carbon #2 Carbon #3 Carbon #4 Carbon #6	Carbon #4 Carbon #5 Carbon #6	Carbon #3
Ash-based Catalysts	Subbituminous Ash #5	Subbituminous Ash #5	-
Metal-based Catalysts	Pd #1 Pd #3 (Pd #2 not tested)	Pd #1 Pd #2 Pd #3	Fe #1 Pd #1 SCR (Pd #2 and Pd #3 not tested)

Long-term Test Results

Site 1

Based on screening test results, the following materials were selected for long-term testing at Site 1: Carbon #1, Carbon #4, Carbon #6, and Subbituminous Ash #5. All four exhibited high oxidation percentages of elemental mercury (93 to 100%) in the short-term screening tests. Table 3-8 illustrates how these materials were configured in the catalyst test unit. The long-term test commenced in May 1998, with the heated box temperature set at 300°F and the flow rate through each cell set at 5 L/min (as measured downstream at ambient temperature).

As noted in Table 3-8, one of the six beds contained only sand to serve as a blank, and one test cell had two beds containing the same catalyst material (Carbon #1) in series. Also note that the activated carbon materials were tested at lower dosages than the other materials due to their higher activity as observed in short-term testing.

Table 3-8
Initial Catalyst Configuration for Long-term Testing at Site 1

	Test Cell #1	Test Cell #2	Test Cell #3
Packed Bed A	75 g of sand	250 mg Carbon #1 in 75 g sand bed	250 mg Carbon #6 in 75 g sand bed
Packed Bed B	1500 mg Subbituminous Ash #5 in 75 g sand	250 mg Carbon #1 in 75 g sand bed	250 mg Carbon #4 in 75 g sand bed

The semi-continuous analyzer described in Section 2 is not automated to allow continued unmanned operation. Therefore, throughout this project, catalyst oxidation measurements were only made when project team members returned to the site to operate the analyzer and collect mercury concentration data.

After putting the catalysts in service at the end of May, the first return trip to Site 1 was made at the end of June, after the catalyst materials had seen about five weeks of flue gas exposure. All of the catalysts showed some loss of activity relative to short-term test results. The second sampling trip was in mid-July, after seven weeks treating flue gas. The catalyst outlet elemental mercury measurements during this trip indicated that the loss of activity was even greater. Of the five catalyst beds, only the second, downstream Carbon #1 bed and Carbon #6 bed (which was in the upstream position) retained any activity. The oxidation percentages measured across these two beds were low, at 26 and 13%, respectively, while the other three beds showed no measurable oxidation of elemental mercury.

It was decided to restart the test with an order of magnitude greater catalyst content in the sand beds. The two experimental carbons, Carbon #6 and Carbon #4, were replaced with commercially available Carbon #2, that had seen success in other testing, and the commercially available palladium catalyst material (Pd #1). The latter was to provide more diversity in the catalyst types being tested, in case the carbon-based catalysts were specifically affected by a component in the Site 1 flue gas. In the initial catalyst screening tests at Site 1, the palladium-based catalyst was observed to achieve 90% oxidation of elemental mercury across two beds (although at only 6% of the total catalyst mass loading used in the second long-term test), while Carbon #2 achieved essentially 100% oxidation. The catalyst configuration for the restart of the long-term test at Site 1 is summarized in Table 3-9.

Table 3-9
Second Catalyst Configuration for Long-term Testing at Site 1

	Test Cell #1	Test Cell #2	Test Cell #3
Packed Bed A	2.5 g Carbon #1 in 75 g sand bed	75 g of sand	15 g Pd #1 in 75 g sand bed
Packed Bed B	2.5 g Carbon #1 in 75 g sand bed	14 g Subbituminous Ash #5 in 75 g sand bed	2.5 g Carbon #2 in 75 g sand bed

This catalyst charge remained in operation for the remainder of the long-term test period, approximately 5 months. This time period amounted to almost 3500 hours of operation and subsequent catalyst exposure to approximately 600 to 620 Nm^3 of flue gas. The catalyst bed oxidation results over this five-month period are summarized in Table 3-10.

The results in Table 3-10 show that the increased catalyst loadings significantly increased catalyst life. After approximately 1000 hours, which is equivalent to when the first test ended, three of the catalyst beds retained substantial activity. The other two were not measured because of analytical difficulties. After approximately 2350 hours, all of the catalysts retained a substantial amount of activity. The Carbon #1 beds retained about half of their original activity, while the other catalysts retained 75% of their original activity or greater. Subbituminous Ash #5

Table 3-10
Results from the Second Long-term Catalyst Test Period at Site 1

Parameter	Measured Results				
	Screening Tests	After 6-7 Weeks	After 14 Weeks	After 18 Weeks	After 21 Weeks
Inlet Total Mercury, $\mu g/Nm^3$	7.0 – 26.1	9.8	15 – 27	31 – 35	27
Inlet Elemental Mercury, $\mu g/Nm^3$	3.7 – 16.2	5.4	8.3 – 9.3	17.8	3.7
Inlet Mercury Oxidation, %	25 – 50	45	45 – 66	49	86
Elemental Mercury Oxidation Across Catalyst Beds, %*					
Sand Blank	3.3 – 8.1	7	9 – 12	23	0
Subbituminous Ash #5	100**	36	82	73	0
Carbon #1 (1st bed)	100**	66	45	0	89
Carbon #1 (2nd bed)	100**	81	42 – 59	0	0
Pd #1	90**	ND	82	0	0
Carbon #2	97**	ND	76	0	76
Catalyst Bed Temperature, °F (°C)	300 (149)	300 (149)	300 (149)	220 (104)	300 (149)
Hours in Operation	24	1000	2300 – 2400	3027 – 3055	3477 – 3488

* All results are corrected to account for the observed mercury oxidation across the sand bed blank.
** Screening test results are for two beds, but at a much lower catalyst loading; total catalyst mass is 6% of the mass in one bed during the second long term test.
ND – not determined due to analytical problems.

showed substantially greater activity than at 1000 hours, which suggests that either the 1000-hour or 2350-hour data were erroneous.

For the latter periods, test equipment and sampling problems make it difficult to interpret the catalyst activity results. At approximately 3000 hours, all but Subbituminous Ash #5 appeared to have lost all of their activity towards mercury oxidation. However, one of the heaters used to maintain the temperature of the box in which the catalysts were located had failed, lowering the catalyst bed temperatures from the desired value of 300°F (149°C) to 220°F (104°C). A suspected mechanism for loss of catalyst activity is that species in the flue gas condense, react and/or adsorb on the catalyst surface, thus blocking active sites for catalysis. The lower temperature that resulted from the failed heat plate would have certainly exacerbated tendencies for flue gas species such as sulfuric acid or selenium to adsorb and/or condense on catalyst surfaces, and may have caused a premature loss of activity.

The heater plate was replaced, and the catalysts were left in operation for an additional 450 hours before the final measurements were made. The final measurements were confounded by an apparent mercury oxidation bias, though. The mercury concentrations at the test unit inlet, as measured by the semi-continuous analyzer, indicated 86% oxidation in the inlet gas. This was a higher oxidation percentage than was ever previously measured at Site 1, and was higher than was measured the next day by the draft Ontario Hydro method. The high oxidation percentage at the test unit inlet suggests either an analytical bias, or oxidation of mercury species across the particulate filter or other components in the sample gas path upstream of the test unit. Subsequent laboratory measurements suggest the former, as elemental mercury was observed to be oxidized as it passed through the pump used for the semi-continuous mercury analyzer in the field; this problem is believed to have been caused by corrosion in the pump after extended use.

Two of the carbon-based catalyst beds showed restored activity after the catalyst operating temperature had been returned to $300^{o}F$ ($149^{o}C$)for 450 hours. However, these results are suspect because of the apparent bias in the oxidation numbers. An imminent boiler outage did not allow time to troubleshoot this bias in the field. Instead, the catalyst materials were recovered and tested in the laboratory for remaining activity in a synthetic flue gas and for the ability to be regenerated.

A performance target for this project has been to achieve at least 70% oxidation of elemental mercury for up to one year of operation, without requiring catalyst regeneration over that time period. The results from Site 1 for Carbon #1 are illustrated in Figure 3-2, and show that catalyst material fell short of the target. With two beds in series, the first long term test period at Site 1 showed that Carbon #1 had a useful life of less than 500 hours, while the second test period (prior to the low temperature excursion) showed a useful life of about 1700 hours. It appears that another order of magnitude increase in catalyst loading would be required for Carbon #1 to approach one year of operation at 70% oxidation of elemental mercury at the conditions tested at Site 1.

Some of the other catalysts tested during the second long-term test period at Site 1 showed greater promise as indicated in Figure 3-3. If the 2350-hour data for Pd #1 and for Carbon #2 can be linearly extrapolated, it appears that these catalysts might have achieved a useful life in the range of 3000 to 4000 hours at the loading tested had the low temperature excursion not occurred. Note that the "time zero" oxidation used for these extrapolations was 100% rather than the screening test results for these two catalyst materials, since the screening tests were conducted at a much lower catalyst loading.

A comparison of the operating conditions for these catalyst beds to design conditions for flue gas NO_X selective catalytic reduction (SCR) catalysts shows that it may not be practical to further increase the amount of catalysts in each bed as a means of extending bed life. This comparison is made in Table 3-11. While the superficial velocity and space velocities through the field unit compare favorably to SCR conditions (i.e., indicate smaller reactor requirements), the area velocities do not. The area velocities for the second long-term test period are nearly two orders of magnitude lower than in the SCR units. The area velocities are calculated as the catalyst material's geometric (external) surface area divided by the flue gas flow rate. If we assume that
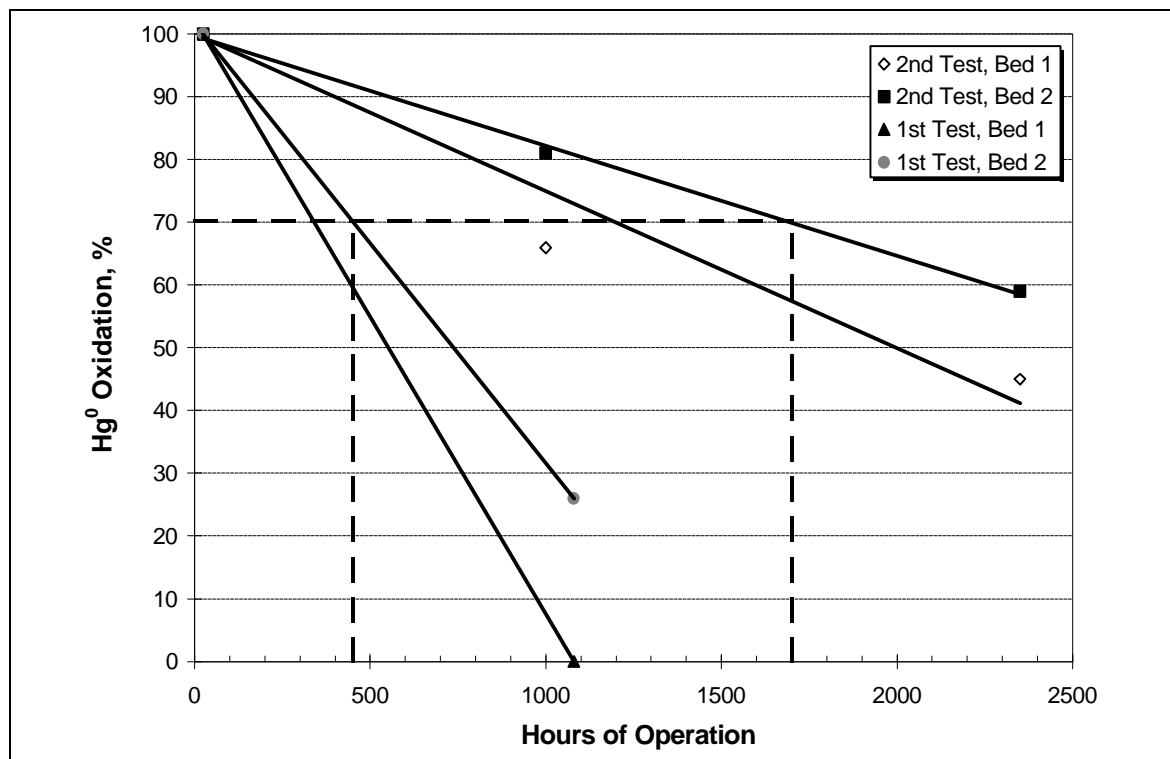
Figure 3-2
Site 1 Catalyst Activity Results for Carbon #1
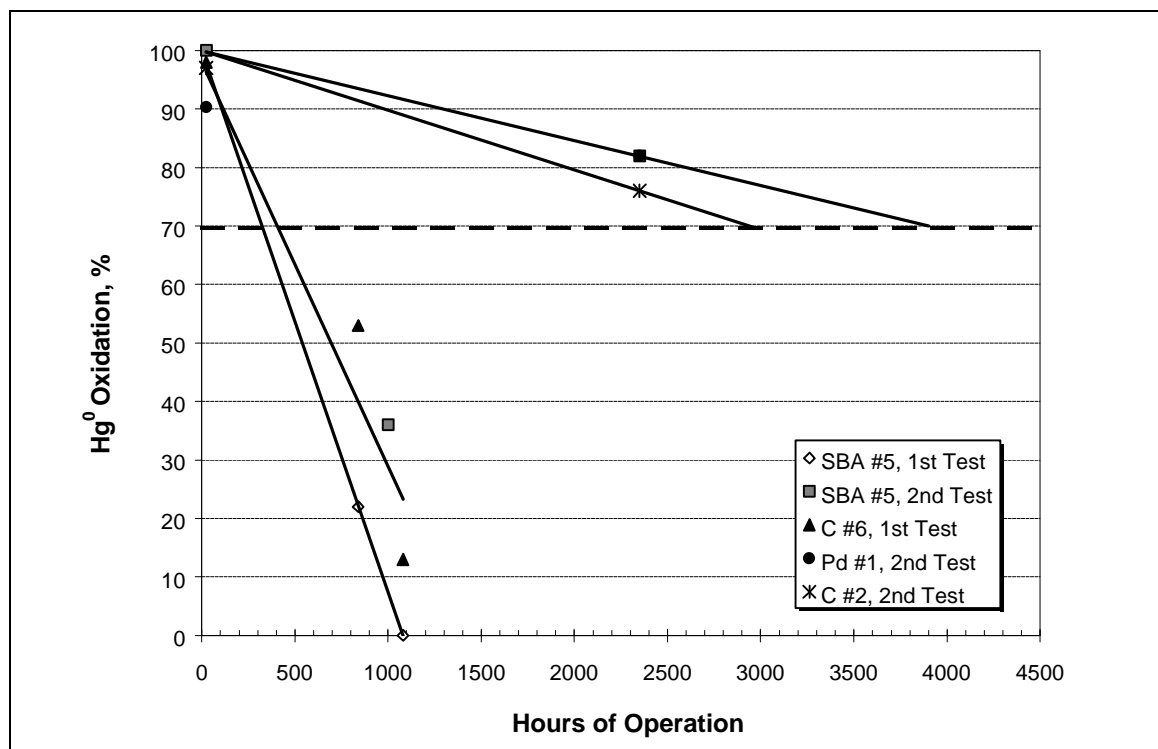
Figure 3-3
Site 1 Activity Results for Various Catalyst Materials

Table 3-11
Characteristics of Two Mercury Catalyst Materials Compared to SCR Catalysts

Catalyst Characteristic	Carbon #1 (two beds)	Pd #1	Range for SCR Catalysts*
Superficial velocity through catalyst bed, ft/sec (m/sec)	0.3 (0.1)	0.3 (0.1)	5.4-12.5 (1.6 – 3.8)
Space velocity, hr^{-1}	50,000**	17,000**	1700-10,300
Area velocity, ft/hr (m/hr)	0.32 (0.10)**	0.22 (0.07)**	13-33 (4 – 10)

* Range reported for EPRI-funded pilot SCR installations at TVA Shawnee Station, NYSEG Kintigh Station, and Niagara-Mohawk Oswego Station.
** Based on the geometric volume and surface area of catalyst materials in test cells; ignores the volume and surface area of sand in each bed.

mercury oxidation occurs primarily on the external surfaces of the catalyst materials (i.e., not in the pores), the area velocity probably represents the best parameter for scaling the sand bed reactor results to a commercially available catalyst bed design. The area velocity comparison in Table 3-11 suggests that a much larger reactor than a typical SCR unit would be required for mercury oxidation, unless a much greater geometric surface area per unit volume of catalyst could be employed than in the honeycomb designs typically used in SCR. After making this comparison, it became apparent that future testing should focus on operating at lower catalyst loading in the sand beds.

Site 2

The long-term test at Site 2 was started in May 1999, but a power outage in June allowed flue gas species to condense on the catalyst surfaces. Because it was early in the test, it was restarted with fresh catalyst material rather than risk adverse effects from this temperature upset. The long-term test at Site 2 was completed in mid-November 1999. At the completion of the long-term test the catalysts had been exposed to flue gas for approximately 3864 hours.

Screening test results were used to identify catalysts for long-term testing at Site 2. Table 3-12 summarizes the catalyst materials and loadings tested at Site 2. Of these, all but Carbon #3 were also previously tested in long-term tests at Site 1. Carbon #3 is an experimental carbon derived from Illinois bituminous coal. Carbon #3 was not one of the three tested in the intermediate-length screening tests for carbon-based catalysts in April. However, the intermediate-length screening test results showed that two of the three tested would be expected to lose activity early in the long-term test. Because it was desired to test two carbon-based catalysts, and because a single bed of Carbon #3 had shown relatively high activity in the short-term tests, it was decided to include Carbon #3 as the fourth catalyst and the second carbon catalyst for the long-term test.

Table 3-13 and Figure 3-4 show catalyst performance data over the long-term test period. The supply of power to the test equipment was interrupted prior to the final day of scheduled testing in November. Analyses of outlet elemental mercury concentrations had been completed for two of the five catalyst beds (Pd #1 and Carbon #3) prior to the power outage. Due to the decrease in

Table 3-12
Catalyst Configuration for Long-term Testing at Site 2

Bed Position	Test Cell #1	Test Cell #2	Test Cell #3
Packed Bed A	250 mg Carbon #6 in 75 g sand bed	75 g of sand	250 mg Carbon #3 in 75 g sand bed
Packed Bed B	250 mg Carbon #6 in 75 g sand bed	3.75g Pd #1 in 75 g sand bed	1.5 g Subbituminous Ash #5 in 75 g sand bed

Table 3-13
Catalyst Performance at the End of the Long-term Test at Site 2

Catalyst	Catalyst Position	Flue Gas Exposure (hours)	Mercury Adsorption Breakthrough (% of Inlet Hg)	Elemental Mercury Oxidation (% of Inlet Hg^0)
Carbon #6 – First Bed*	1A	3192	76**	40
Carbon #6 – Second Bed*	1B	3192	54	78
Pd #1	2B	3864	75	96
Carbon #3	3A	3864	100	0
Subbituminous Ash #5*	3B	3192	66	87

* October results are reported for these catalysts; November results are reported for the remaining catalysts.
** This value appears to be erroneously low, as the breakthrough measured in September and November was 100%.

catalyst temperature and the expected condensation of flue gas moisture and acid gas species on the catalyst beds during the power outage, the other three beds were not analyzed for performance after power was restored. Consequently, oxidation percentages at the end of the test are available for only two of the five catalysts. The adsorption capacities and oxidation results for each catalyst bed in Table 3-13 and Figure 3-4 correspond to the last time at which oxidation results were measured (i.e., November 1999 for Pd #1 and Carbon #3 and October 1999 for Carbon #6 and Subbituminous Ash #5).

November results (at 3864 hours) indicated that Pd #1 showed no signs of significant deactivation, while Carbon #3 appeared to be completely deactivated. After exposure to 583 Nm^3 (583 x 10^3 NL) of flue gas, Pd #1 oxidized 96% of the elemental mercury, while after exposure to 635 Nm^3, Carbon #3 oxidized none.

The remaining results presented in Table 3-13 and Figure 3-4 are from testing conducted in October, after 3192 hours of flue gas exposure. In October, the second bed of Carbon #6 was achieving 78% oxidation of elemental mercury after having been exposed to 478 Nm^3 (478 x 10^3 NL) of flue gas. The upstream, 250-mg bed of Carbon #6, which had begun to show measurable deactivation after about 1500 hours and exposure to 209 Nm^3 of flue gas, was oxidizing 40% of
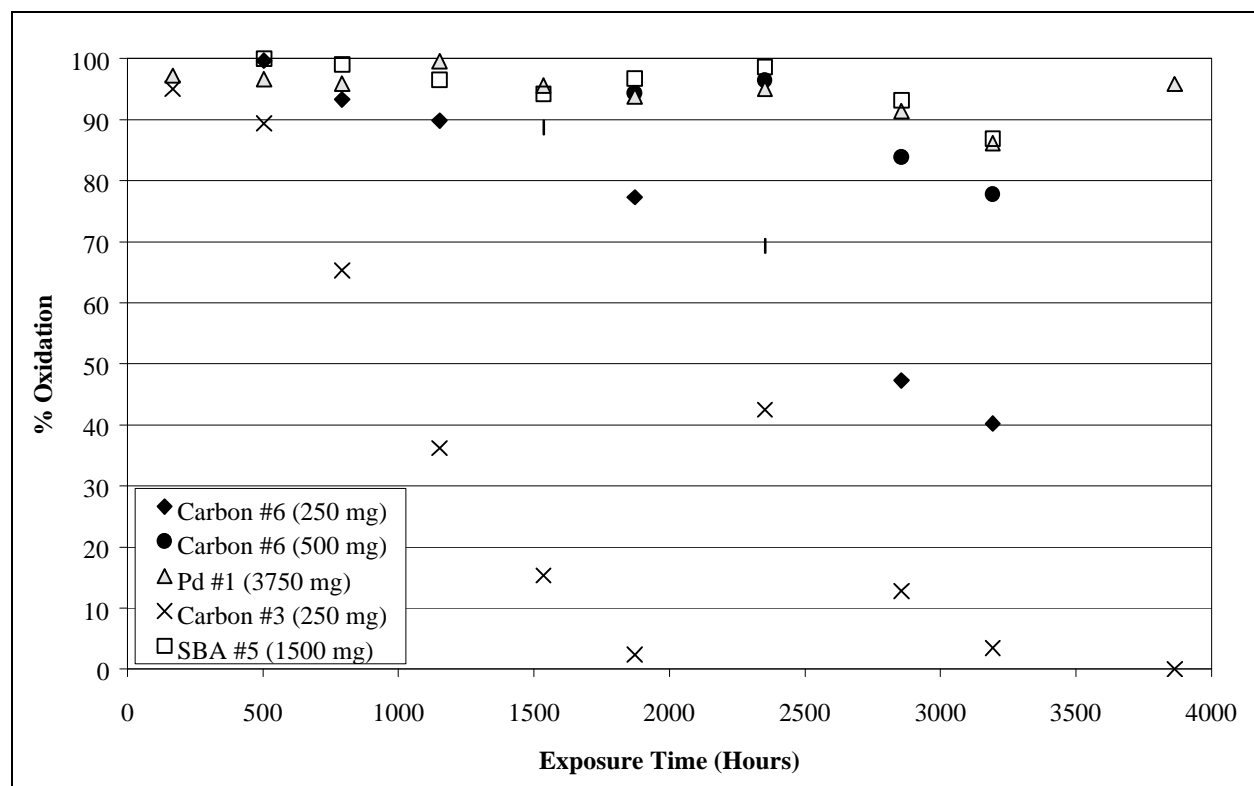
Figure 3-4
Effect of Flue Gas Exposure on Elemental Mercury Oxidation Activity at Site 2

the elemental mercury. The second bed started showing signs of deactivation at about twice the exposure time and gas volume as the first bed, which suggests that deactivation occurred across the two beds in a linear relationship with the amount of flue gas treated.

The results in Figure 3-4 show that mercury oxidation by Carbon #3 began to decrease steadily after about 500 hours and exposure to 74 Nm^3 of flue gas; Carbon #3 only showed 2% elemental mercury oxidation at the end of August (1900 hours). However, Carbon #3 measured 43% oxidation in mid-September (2400 hours). Results from late October (3192 hours) showed only 3% mercury oxidation, suggesting that the September results reflected a measurement error. Measurements made in November confirmed that Carbon #3 was completely deactivated. The Subbituminous Ash #5 catalyst showed 87% oxidation in October, after 3192 hours and 515 Nm^3 of flue gas exposure.

It was an important finding that over the long-term test period, three of the five catalyst beds were able to achieve greater than 70% oxidation of the inlet elemental mercury. Of these, two (Carbon #6 and Subbituminous Ash #5) had begun showing signs of loss of activity. These two may not have been able to achieve the objective of this project of identifying catalysts that would achieve at least 70% oxidation for one year or greater. However, the Pd #1 catalyst was still achieving 96% oxidation after greater than 5 months in service, and showed no measurable trend for decreased activity with time.

Site 3

The screening test results described above were used to identify catalysts for long-term testing at this site. Based on those results, the catalysts listed in Table 3-14 were selected for long-term testing at Site 3.

Table 3-14
Catalyst Materials Selected for Testing in the Long-term Test at Site 3

Bed Position	Test Cell #1	Test Cell #2	Test Cell #3
Packed Bed A	3.75 g Pd #1 in 75 g sand bed	75 g of sand	250 mg Carbon #6 in 75 g sand bed
Packed Bed B	3.75 g Pd #1 in 75 g sand bed	3.75g Fe #1 in 75 g sand bed	1.5 g Subbituminous Ash #5 in 75 g sand bed

The Pd #1 catalyst and Subbituminous Ash #5 were shown to be active at other sites, particularly Site 2, and thus were chosen for long-term testing at Site 3. The decision to test Subbituminous Ash #5 was made in spite of the fact that it did not show high activity in the results from short-term Test 2. The results of short-term Test 1 showed another metal-based catalyst, Fe #1, was also active in the bituminous coal flue gas. Since an Fe #1 catalyst would be much less expensive to produce than a palladium-based catalyst, this material was also selected for long-term testing. Carbon #6 was selected for the long-term test over Carbon #3, which had showed higher activity at the end of short-term Test 3, based on previous Site 2 results. Carbon #3 was highly active initially at Site 2, but lost activity rapidly over the first few weeks of flue gas exposure. Carbon #6 retained a substantial amount of its original activity over the course of the long-term test at Site 2. Although the mechanisms for catalyst deactivation may be different for Powder River Basin coal versus eastern bituminous coal, it was feared that Carbon #3 would similarly lose activity at Site 3. Thus, it was a judgement call by the project team to select Carbon #6 for the long-term test. Its concentration in the sand bed was increased from 150 mg per 75 g of sand bed in the short-term test to 250 mg per 75 g in the long-term test. This concentration matches the concentration tested at Site 2, and would presumably produce a higher mercury oxidation percentage across the bed at Site 3.

The long-term catalyst test began in mid-July 2000. A few days later, it was discovered that the temperature in the catalyst holder box had dropped to approximately 200°F (93°C) due to failed wiring to some heating elements in the box. The wiring was repaired, and the test was restarted with fresh catalyst materials. Due to a dwindling supply of the Pd #1 catalyst material, when the test was restarted, bed 1A was charged with only 2.0 g of Pd #1 in the 75 g sand bed and the second bed was reused from the initial charge. It was thought that the second bed would have been "protected" from any condensing species by the first bed during the temperature disruption, and therefore should retain high activity.

The early (one-month) performance of the sand bed catalysts being evaluated in the long-term test would have normally been conducted in early- to mid-August. This testing was delayed because an unplanned host unit outage from August 2 to August 19 caused the catalyst test unit to draw only heated air instead of flue gas through the catalyst beds for that time period. Because

the catalysts were purged with air (instead of flue gas) at 300°F (149°C) during this outage, which may have effectively "regenerated" them, it was decided to wait until at least one month after the outage to conduct initial catalyst performance tests.

Three interim site visits were carried out during the long-term test, the first week of October, the third week of November, and the third week of December 2000. The long-term test ended the last week in January 2000. However, because of an apparent analytical bias, the November results represent the last measurable oxidation performance data for the long-term test catalyst materials. This apparent bias is described further below. The November tests represent catalyst results obtained after almost 18 total weeks of flue gas exposure, including the 2 weeks before the outage, but just over 13 weeks of exposure (approximately 2200 hours) after the plant outage.

Table 3-15 lists results for mercury adsorption and oxidation by the catalysts measured during the November trip. The inlet mercury concentration varied between approximately 14 and 20 µg/Nm^3 during this measurement period. The inlet elemental mercury concentration was measured to be only 1.2 µg/Nm^3 during this measurement period, which is well below the value of 3 to 4 µg/Nm^3 measured by the Ontario Hydro method at this site in July 2000.

Table 3-15
November Mercury Adsorption and Oxidation Data from the Long-term Test at Site 3

Catalyst Material	Catalyst Position	Flue Gas Exposure (hours since August outage)	Mercury Adsorption Breakthrough (% of Inlet Hg)	Elemental Mercury Oxidation (% of Inlet Hg^0)
Pd #1 – First Bed	1A	2200	*	87**
Pd #1 – Second Bed	1B	2200	75	***
Sand	2A	2200	86	36
Fe #1	2B	2200	81	45
Carbon #6	3A	2200	84	85**
Subbituminous Ash #5	3B	2200	87	***

*   Not measured because of high observed Hg breakthrough at 8 weeks, and because of high observed Hg breakthrough in current tests on the downstream bed. The assumed value is at or near 100%.
**   These values are corrected to account for the observed reduction in elemental mercury concentration across the sand "blank" in position 2A.
*** Downstream fixed bed concentration not measured due to high oxidation across upstream bed.

Most of the catalysts showed low levels of mercury adsorption. The outlet of the first bed of Pd #1 was not measured; in October it showed less than 10% adsorption. The second bed appeared to adsorb 25% of the inlet mercury. The other beds showed less than 20% mercury adsorption. These results suggest that total breakthrough across these beds had not yet occurred, although several were approaching that point. However, a significant fluctuation in inlet mercury concentration was generally observed in measurements made on the Site 3 flue gas, so it was difficult to quantify breakthrough to greater accuracy than about plus or minus 20%. A bed inlet mercury concentration could easily vary by this amount while the outlet concentration was being

measured. Consequently, it is not possible to determine with certainty which beds had achieved adsorption equilibrium and which had not.

In the oxidation results, the upstream ("A" position) Pd #1 and Carbon #6 samples showed elemental mercury oxidation percentages of 85% or more. Both of these percentages are corrected for the observed elemental mercury adsorption and/or oxidation across the sand bed "blank" in the 2A position. Results for the Fe #1 catalyst indicated 45% oxidation after 14 weeks versus 57% oxidation after 8 weeks of flue gas exposure, again taking into account observed elemental mercury oxidation and/or adsorption across the sand blank. This indicates that deactivation of this sample was continuing to occur. Because of the high oxidation levels measured and subsequent low levels of elemental mercury in the effluent gas from the Pd #1 and Carbon #6 catalysts, tests were not performed on their downstream beds ("B" positions).

Performance results could not be measured during the next trip to Site 3 in December for a number of reasons, including:

- The gas flow through the Pd #1 catalyst sample beds was observed to be plugged at the downstream flow measurement orifice, making the results from measurements on the outlet gas from these beds invalid because of the stagnate flow conditions;

- The inlet sample elemental mercury concentrations were very low (<1 µg/Nm^3), approaching the detection limit for the field mercury analyzer, which made measurement of catalyst outlet concentrations difficult;

- The field mercury analyzer output was relatively noisy during this sampling period, for reasons unknown, making it more difficult than normal to accurately measure elemental mercury concentrations below 1 µg/Nm^3; and

- The sand blank bed in position 2A appeared to adsorb and/or oxidize a relatively high percentage of the already low inlet elemental mercury content, making the adjusted inlet elemental mercury concentrations to the other beds even lower.

The low inlet elemental mercury concentration of about 0.9 µg/Nm^3 measured in December 2000 corresponds with a very high mercury oxidation percentage of 94%. This was a much higher oxidation percentage than was observed during the initial testing at Site 3 in June 2000 (62 to 70%).

The last site visit at Site 3 was carried out the weeks of January 22 and January 29, 2001. Testing at Site 3 was concluded at the end of this test period. The January measurements would represent catalyst results obtained after 27 to 28 total weeks of flue gas exposure, including the 2 weeks before the outage, but only about 23 weeks of exposure after the plant outage. However, no results were measured in January for mercury oxidation across the catalyst beds, for the same reasons that impacted the December measurements.

Consequently, there are no end-of-test mercury oxidation results to report. In retrospect, the ability to measure catalyst mercury oxidation performance at Site 3 were confounded by two ongoing effects that become apparent when reviewing and analyzing the long-term test performance data. First, the elemental mercury concentrations measured with the field analyzer

at the inlet to the long-term test apparatus were observed to decrease almost linearly with time. This effect is illustrated in Figure 3-5. Note, however, that the elemental mercury concentrations measured by the draft Ontario Hydro method at the beginning and end of the long-term test period do not show a similar downward trend; the same value of 3 to 4 µg/Nm^3 was measured both times.

Second, the apparent oxidation percentage across the sand bed blank was observed to increase with time. This effect is illustrated in Figure 3-6. The net of these two effects is that there were not sufficient elemental mercury concentrations measured at the long-term test apparatus to measure catalyst performance at Site 3 after the November measurement trip.

Figure 3-7 illustrates the catalyst oxidation results available from the long-term test at Site 3, which are limited to short-term test data and results measured in October and November. The results plotted in Figure 3-7 show that the upstream Pd #1 catalyst and Carbon #6 remained active (greater than 80% oxidation of elemental mercury) through approximately 2200 hours since the August outage was over (almost 4000 hours since the long-term test began). Fe #1 catalyst had begun to lose activity (less than 50% oxidation of elemental mercury). No results are available for the downstream bed of Pd #1 or for Subbituminous Ash #5, because those beds were downstream of beds that remained at high oxidation activity through at least November. The catalyst bed materials were recovered at the end of the test, and laboratory tests were conducted to measure end-of-test catalyst performance in a simulated flue gas (see Section 4).

No reason has been identified as to why the elemental mercury concentrations measured by the field analyzer in December and January were too low to allow evaluation of catalyst performance, in spite of the fact that in January sampling by the Ontario Hydro method showed much higher elemental mercury concentrations. Quality control measures employed to improve analyzer performance included:

- Replacing a quartz probe liner in the flue gas duct;
- Replacing Teflon$^®$ sample lines;
- Ensuring that all sample lines were adequately heat traced and that no moisture was condensed in the lines;
- Cleaning all fly ash from the long-term test apparatus filter upstream of the catalyst beds;
- Cleaning and/or replacing impingers in the analyzer sampling train;
- Replacing impinger solutions;
- Replacing the gold in the adsorption portion of the analyzer; and
- Recalibrating the analyzer with an elemental mercury standard.

None of these efforts were found to affect the elemental mercury concentrations measured by the field analyzer at the FGD inlet location. It is speculated that apparent bias in the sample gas was real and not a gas analysis problem, most likely caused by a buildup of a high-LOI Site 3 fly ash in the apparatus that resulted in elemental mercury adsorption and/or oxidation in the sample gas.
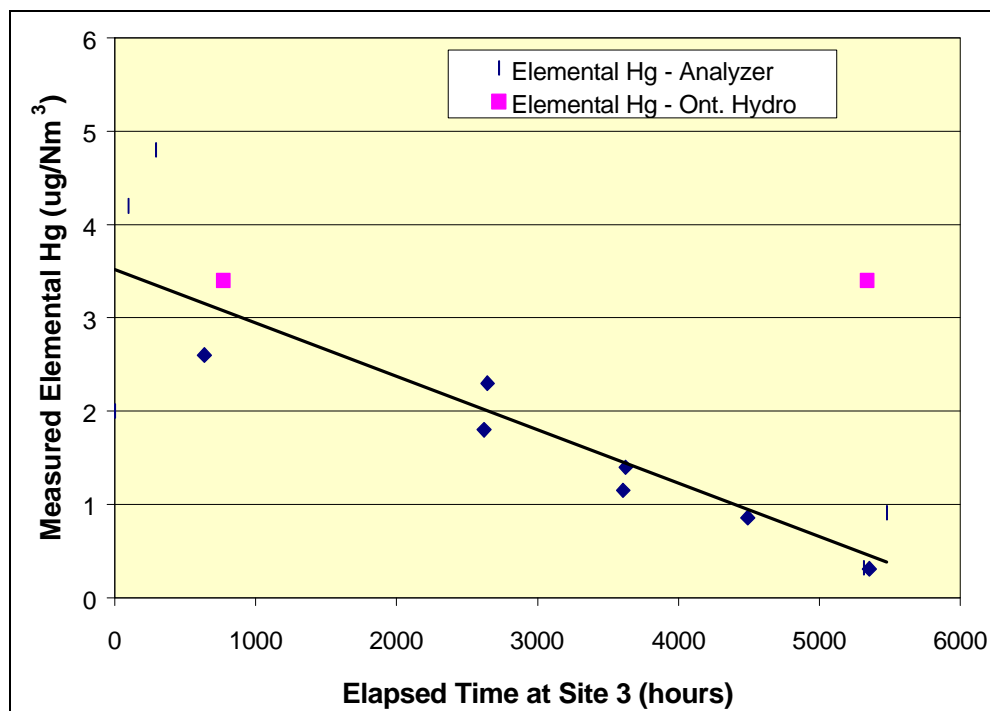
Figure 3-5
Observed Decrease in Measured Elemental Mercury Concentrations with Time at Site 3
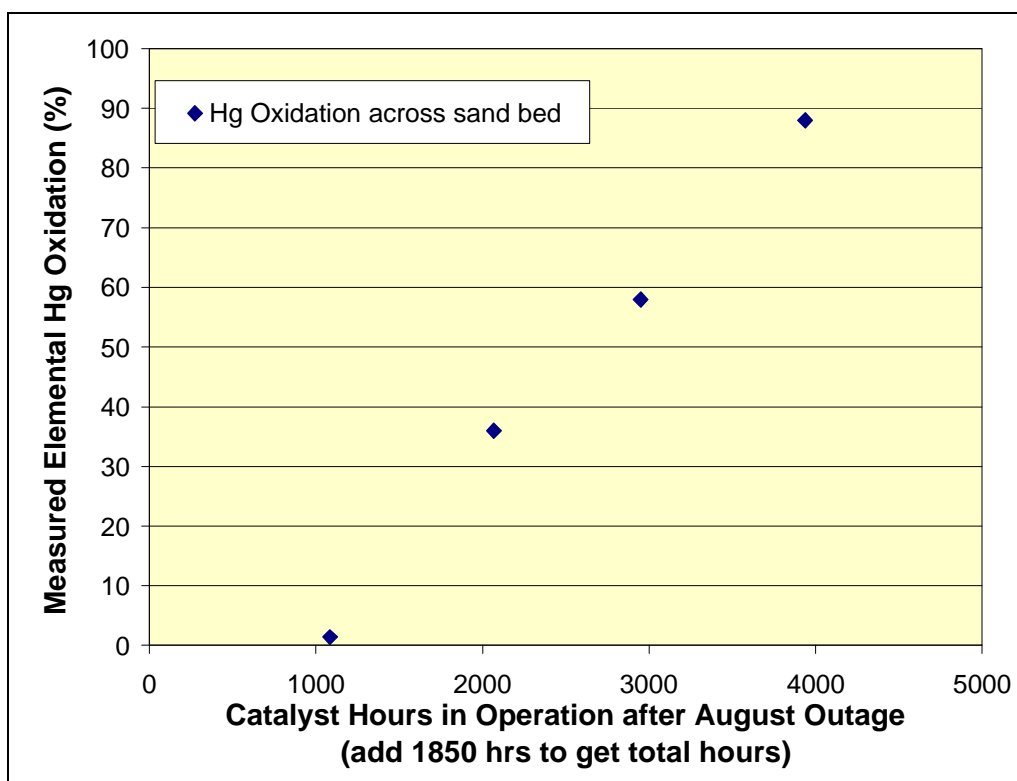
Figure 3-6
Apparent Elemental Mercury Oxidation Percentage vs. Time in Operation for the Sand Bed Blank in the Long-term Test Apparatus
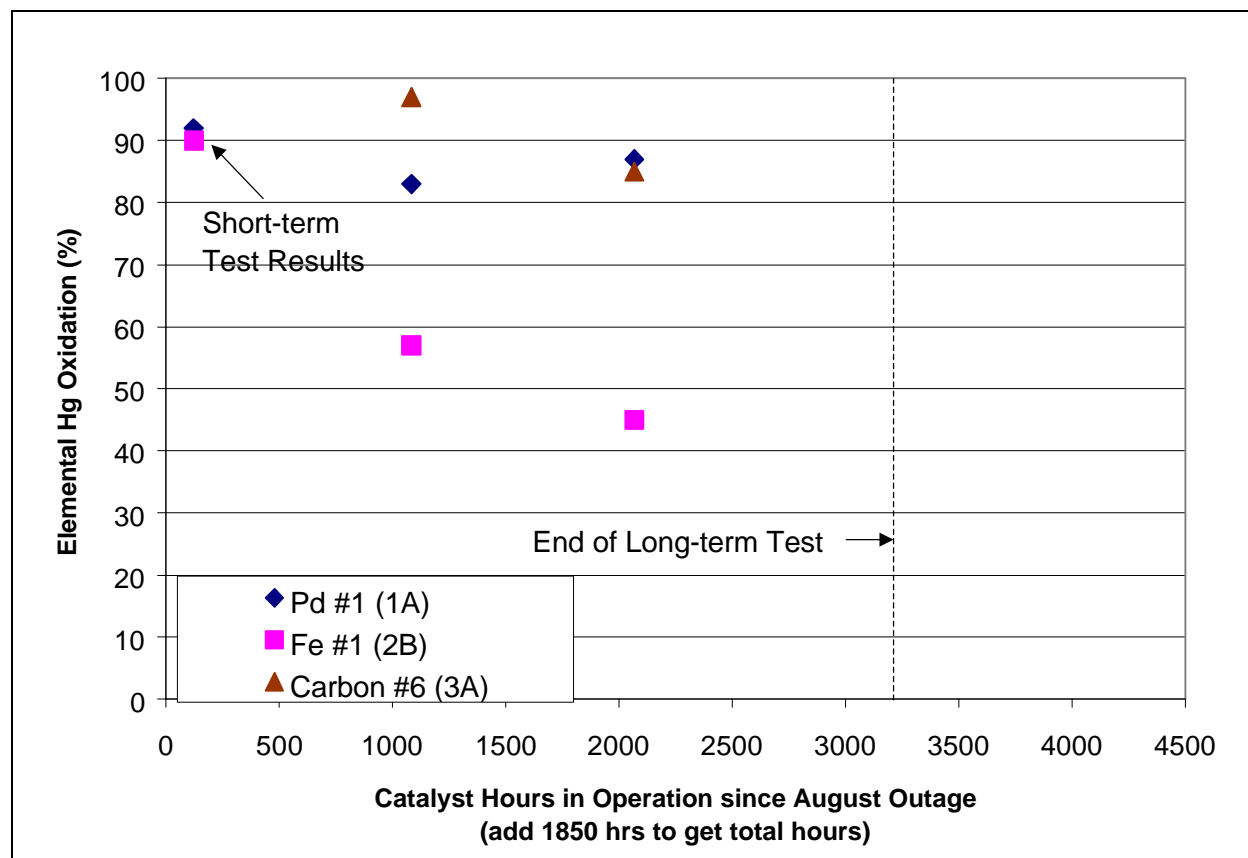
Figure 3-7
Long-term Catalyst Oxidation Results from Site 3

Commercial Catalyst Form Tests

During the long-term testing of catalyst sand beds at Sites 2 and 3, additional tests were conducted to evaluate the activity of catalysts in commercially available configurations rather than as the finely ground powders dispersed in sand tested in the long-term test apparatus. Configurations tested included honeycomb supports (such as those used in SCR) and extruded pellets.

The objective of these tests was to evaluate promising catalysts identified in the long-term tests in commercially available configurations and at area velocities consistent with reactor sizes used in the utility industry or smaller. SCR catalysts typically operate at area velocities ranging from 15 to 30 standard ft/hr (4 to 9 Nm//hr). If mercury catalysts prove effective at similar or higher area velocities, it is likely that honeycomb support structures could be utilized in a reactor of a commercially viable size. Also, mercury oxidation catalysts operated downstream of the particulate control device (e.g., in clean gas) could employ a much tighter honeycomb pitch than in typical SCR applications. This would allow smaller reactor sizes at a given area velocity.

Pellet Catalyst Form Tests

During the long-term test at Site 2, a number of tests were conducted to compare the performance of the Pd #1 catalyst in pellet form to that in the sand bed reactor. Table 3-16 compares the area velocities, adsorption breakthrough and oxidation percentages associated with Pd #1 in the sand bed reactor of the long-term test at Site 2 to those for the pellet reactors.

Table 3-16
Area Velocities Tested for Pd #1 at Site 2

Catalyst Form	Catalyst Mass (g)	Area Velocity (std. ft/hr [Nm/hr])	Flue Gas Exposure (Nm^3)	% Breakthrough of Total Hg	% Oxidation of Elemental Hg
Sand Bed	3.75	165 [48]*	583	75	96
Pellet	40	110 [32]	370	77	95
Pellet	20	210 [61]	402	100	97
Pellet	10	430 [120]	175	-	77
Pellet	5	860 [250]	323	86.3	67

* Area velocity estimated based on amount of palladium present in the sample. This assumes that the palladium is present at the surface of the ground Pd #1 beads at a percentage of the total particle surface area that is equivalent to the mass fraction on the original pellets.

The first pellet reactor test was conducted with 40 g of pellets in the reactor and a flue gas flow rate of 27 NL/min, and showed very high oxidation after two weeks of flue gas exposure. Subsequently another two-week test was conducted with a 20-g bed of Pd #1 pellets at a similar gas flow rate, resulting in twice the area velocity of the first test, at 210 standard ft/hr (61 Nm/hr). After two weeks, this second test showed that the catalyst had reached adsorption equilibrium and was oxidizing greater than 97% of the elemental mercury. A set with 5 g of pellets was subsequently exposed to flue gas at a similar rate for a similar time period, resulting in an area velocity of 860 standard ft/hr (250 Nm/hr). At this high area velocity mercury oxidation dropped to about 67%. To pinpoint the maximum area velocity at which high oxidation efficiency could be achieved, a test of a 10-g sample was conducted. Results from that test showed 77% oxidation of the elemental mercury in the treated gas. Mercury adsorption could not be measured due to analytical problems.

These results show that greater than 70% mercury oxidation was achieved at an area velocity over an order of magnitude greater than that typical of SCR catalysts, and nearly 100% oxidation was achieved at an area velocity about seven times greater. The results suggest that high mercury oxidation efficiencies could be achieved with a reactor much smaller than is typically required for SCR applications, if similar performance could be achieved with a honeycomb catalyst.

Honeycomb Catalyst Structure Tests – Site 2

To evaluate the effect of catalyst geometry on performance, the Pd #1 catalyst was obtained coated on a honeycomb structure. The honeycomb, wash coated with the same material as the Pd #1 pellet catalyst, has dimensions based on those used in "clean side" SCR applications: a cell density of 64 cpsi, a 3.2-mm pitch, and a geometric surface area of about 340 ft^2/ft^3 (1100 m^2/m^3).

During the last two months of the long-term test at Site 2, mercury oxidation tests were also conducted with 2-inch-long (51-mm) honeycomb structures. The structures were arranged in sets of two in series and exposed to flue gas at area velocities ranging from 74 to 260 standard ft/hr (21 to 75 Nm/hr). The superficial velocities ranged from 2.3 to 4.5 standard ft/sec (0.7 to 1.3 Nm/sec). Results from one set of tests are summarized in Table 3-17.

Table 3-17
Performance of Pd #1 on a Honeycomb Structure at Site 2

Catalyst Position	Area Velocity (std ft/hr [Nm/hr])	Superficial Velocity (std ft/sec [Nm/hr])	Flue Gas Exposure*		Mercury Adsorption Breakthrough (% of Total Hg)	Elemental Mercury Oxidation (% of Hg^0)
			Hours	Nm^3		
2a	190 [55]	3.3 [1.0]	961	910	73	51
2b	110 [32]	3.3 [1.0]	962	910	69	56

* Estimated.

Because of a malfunctioning pump in the test apparatus, the actual amount of flue gas exposure for the catalysts is uncertain. The time of the pump failures was estimated as halfway between times when flow was verified. Based on this assumption, honeycomb catalyst set #2 achieved 51 to 56% oxidation after exposure to 909 Nm^3 of flue gas, at area velocities of 190 and 110 standard ft/hr, respectively (55 and 323 Nm/hr).

The oxidation by the honeycomb catalysts did not compare well with the oxidation by the Pd #1 pellets at similar area velocities. Whereas at 190 standard ft/hr the honeycomb oxidized 51% of the elemental mercury, at a slightly higher area velocity of 210 standard ft/hr (61 Nm/hr) the Pd #1 pellets showed 97% oxidation. The negligible deactivation of Pd #1 in the long-term sand bed test suggests that loss of activity due to flue gas exposure would not be the cause of the lower oxidation. Two possible explanations for the lower performance of the honeycomb catalyst structure were hypothesized: 1) Insufficient catalyst loading on the honeycomb surface (e.g., insufficient loading of palladium on the honeycomb to ensure complete coverage of the alumina substrate and very high surface reaction rates), or 2) Inadequate flue gas contact with the catalyst surface. The latter could be a result of diffusion of elemental mercury from the bulk flue gas to the honeycomb surface controlling the overall reaction rate.

To determine what factor had a detrimental effect on oxidation, honeycomb samples with greater catalyst loadings were tested to determine if increased oxidation resulted at higher palladium

loading. These results are presented in Section 4, but they did, in fact, show higher oxidation percentages when the palladium loading was increased.

In parallel, mass transfer calculations were conducted to model elemental mercury conversion in the honeycomb reactor versus the pellet reactor. For these calculations, the reaction rate was assumed to be instantaneous at the catalyst surface (i.e., reaction kinetics were assumed not to control the overall reaction rate). These calculations were intended to indicate the extent to which mercury diffusion from the flue gas to the honeycomb surface controls the overall conversion, relative to that for the pellet reactor.

The results of these calculations showed that mercury diffusion rates did impact the performance of the honeycomb catalyst relative to the pellet catalyst beds at Site 2. They showed that at similar area velocity values, the predicted mercury oxidation was higher for the pellet bed than for the honeycomb, with the honeycomb performance being limited by the rate of mercury diffusion to the honeycomb surface. For example, at an area velocity of 210 standard ft/hr (61 Nm/hr), the predicted mercury performance for the pellet catalyst was very near the observed value, at 98% oxidation. For the honeycomb at a somewhat lower area velocity of 190 standard ft/hr (55 Nm/hr), the predicted mercury oxidation was only 78%.

The calculation results also show that the measured performance of the honeycomb catalyst fell short of the predicted mercury oxidation based on "instantaneous" oxidation at the surface, with a predicted value of 78% versus a measured value of 51%. The measured pellet catalyst results nearly equalled the predicted results for that configuration (97% versus 98%). This was further indication that the palladium loading on the honeycomb surface was not sufficient to provide nearly instantaneous reaction rates.

Honeycomb Structure Tests – Site 3

Subsequent honeycomb catalyst testing at Site 3 provided an opportunity to demonstrate improved honeycomb performance at a higher palladium loading on the alumina substrate. A honeycomb catalyst test at Site 3 was started in July 2000. In these tests, two 2-inch (51-mm) lengths of Pd #1 catalyst in series were placed in service in a separate 300°F (149°C) hot box, installed at the FGD inlet location beside the long-term sand bed test apparatus. This second hot box was set up to pull a flue gas sample through a separate probe from that for the long-term sand bed apparatus.

The honeycomb samples were prepared at three times the palladium loading tested at Site 2 (30 g/ft^3 or 850 mg/m^3 loading versus 10 g/ft^3 or 280 mg/m^3 at Site 2). The higher loading was selected based on laboratory results that showed this loading being adequate to ensure high activity of the wash-coated honeycomb catalyst. The alumina substrate was the same as was tested at Site 2.

Evaluation of the honeycomb samples was not possible during the first return sampling trip to Site 3, in October 2000, due to an equipment problem. The honeycomb sample hot box was repaired during the next site visit in November and the honeycomb catalyst test was restarted at that time. Because the hot box had been at low temperature for some time, presumably allowing

condensable species in the flue gas to foul the catalyst surface, the honeycomb catalyst test was restarted with fresh honeycomb samples after the hot box was repaired. Initial catalyst performance measurements were made the next day. Table 3-18 summarizes the mercury adsorption and elemental mercury oxidation data for these samples.

Table 3-18
November Mercury Adsorption Data from the Honeycomb Sample Test at Site 3

Catalyst Material	Honeycomb Catalyst Position	Approximate Area Velocity (sft/hr [Nm/hr])	Observed Hg Breakthrough (%)	Observed Elemental Hg Oxidation (%)
Pd #1 Honeycomb Sample 1	1A	170 [49]	81*	70
Pd #1 Honeycomb Sample 2	1B	170 [49]	136*	21**
Two Beds in Series	1B	86 [25]	~100	76

* The outlet concentration from the second honeycomb was measured to be higher than the inlet of the first honeycomb in series; this is taken as evidence of inlet mercury variation and that both samples are essentially at adsorption equilibrium.

** Both the inlet and outlet concentrations for this sample are near the detection limit for the field analyzer; the observed percent oxidation of elemental mercury across this sample may not be a meaningful value.

The mercury adsorption data in Table 3-18 suggest that both honeycomb samples were at adsorption equilibrium. The outlet total mercury concentration from the second honeycomb sample in series was greater than the concentrations measured at the inlet or the outlet of the upstream sample, but within the range of total mercury concentrations measured for the Site 3 flue gas during this trip. This suggests that the measured concentrations represent little or no mercury adsorption, just normal mercury concentration fluctuations in the inlet flue gas.

The elemental mercury oxidation data in Table 3-18 show that the honeycomb samples were active. However, the low inlet elemental mercury concentrations measured make it difficult to quantify the oxidation percentages being achieved. Particularly for the second honeycomb in series, the inlet and outlet elemental concentrations were measured to be less than 0.5 μg/Nm^3, which is near the detection limit of the analyzer, so the percent reduction value shown in the table is of questionable accuracy.

The observed 70% oxidation for the first honeycomb compares well with a conversion of 80% predicted using a previously developed mass transfer model that assumes instantaneous oxidation when mercury contacts the honeycomb surface. The effective area velocities for these catalysts are approximately 170 standard ft/hr (49 Nm/hr) for each sample individually, and 86 standard ft/hr (25 Nm/hr) for the two in series. Note that at Site 2, the palladium/alumina honeycomb achieved only 51% oxidation at a similar area velocity of 190 standard ft/hr (55 Nm/hr) with one 2-inch (51-mm) honeycomb length, and 56% at an area velocity of 105 standard ft/hr (30 Nm/hr) with two 2-inch (51-mm) lengths in series. These results from Site 3 indicate that increasing the palladium loading by a factor of three over the loading tested at Site 2 was effective at improving honeycomb mercury oxidation performance.

Flue Gas Characterization Results

Site 1

Earlier in this section, Table 3-1 summarized the flue gas conditions at Site 1 measured at the beginning of the long-term test period in May 1998, and at the end in December. Results from measurements during Phase I of this project were also included for comparison. Over this period of time, both the flue gas SO_2 concentrations, as measured by the plant continuous emissions monitoring (CEM) system, and flue gas mercury concentrations measured by the project team were observed to vary significantly.

The plant reports that SO_2 concentrations are known to vary widely depending on lignite quality as delivered from the mine. However, these data provided a first indication that mercury levels in the lignite vary significantly as well, as the testing at Site 1 preceded the EPA ICR program. Coal mercury concentrations measured in May and December 1998 substantiated that the observed variability was due to changes in coal mercury content and not sampling and analytical variability. The coal mercury content was observed to vary by almost a factor of two between the May and December samples. An attempt was made to close mass balances between the coal mercury and the mercury accounted for in the FGD inlet flue gas. These mass balance results are summarized in Table 3-19.

The mass balance closures of 85 and 122% are for all practical purposes within the desirable range (100% ±20%) for trace metals measurement around a full-scale power plant. A closure of greater than 100% indicates that more mercury was accounted for in the flue gas at the FGD inlet and in the ESP ash than can be accounted for by the mercury in the coal fired, while a closure less than 100% indicates the opposite situation.

Measurements were also made at the FGD outlet in May and December 1998. Past experience (and more recent EPA ICR data) has shown that wet FGD systems efficiently remove oxidized forms of mercury, but remove little if any elemental mercury. If this holds true, flue gas mercury measurements at the FGD system outlet provide an indication of the accuracy of the elemental mercury concentrations measured at the ESP outlet (FGD system inlet).

This comparison is made in Table 3-20, for the average of three runs each in May 1998 and December 1998. The results for May 1998, made with Method 29T, show the expected result, that elemental mercury concentrations at the FGD outlet location are similar to those measured at the inlet, and that 98% of the oxidized mercury appears to have been removed by the FGD system. The December 1998 results, measured with the draft Ontario Hydro method, do not follow the expected trend. The FGD outlet elemental mercury concentration measured was 40% lower than the elemental mercury concentration measured at the inlet. It is doubtful that this much elemental mercury was removed across the FGD system. The apparent removal of oxidized mercury across the FGD system is high (94%) as expected, though.

The December results suggest that the FGD inlet (ESP outlet) elemental mercury concentration measurement is biased high. The results of the first run in December appear to skew the average. The first run showed an elemental mercury concentration of 25.9 µg/Nm^3 at the inlet, but only

Table 3-19
Results of Mercury Mass Balances at Site 1

Parameter	May 1998	December 1998
Coal mercury content, mg/kg	0.14	0.21
Amount of coal fired, tons/hr (100 kg/hr)*	565 (514)	399 (363)
Mercury in coal fired, lb/hr (g/hr)	0.16 (73)	0.17 (77)
Total mercury concentration in ESP outlet flue gas, μg/Nm^3	17	31
Flue gas flow rate at ESP outlet, dscfm (Nm^3/s)*	1.8×10^6 (850)	1.7×10^6 (800)
Total mercury in flue gas, lb/hr (g/hr)	0.11 (50)	0.19 (86)
Mercury concentration in fly ash, mg/kg	**	0.17
Fly ash collection rate, tons/hr (1000 kg/hr)	72 (65)	41 (37)
Mercury in fly ash collected, lb/hr (g/hr)	0.02 (9)	0.01 (5)
Mercury in bottom ash, lb/hr (g/hr)	0	0
Total mercury accounted for in flue gas and fly ash, lb/hr (g/hr)	0.14 (63)	0.20 (91)
Mercury material balance closure, % of coal mercury accounted for	85	122

* By combustion calculation.
** Not measured; assumed to be equal to December 1998 concentration.

Table 3-20
Comparison of FGD System Inlet and Outlet Elemental Mercury Concentrations

Sampling Method	Sample Location	Elemental Mercury Concentration (μg/Nm^3)	Oxidized Mercury Concentration (μg/Nm^3)	Total Mercury Concentration (μg/Nm^3)	Mercury Oxidation (% of total Hg)
May 1998 Results					
Method 29T	FGD Inlet	4.2	12.9	17.1	76
Method 29T	FGD Outlet	4.8	0.2	5.0	4
December 1998 Results					
Ontario Hydro	FGD Inlet	20.6	10.1	30.6	33
Ontario Hydro	FGD Outlet	12.1	0.6	12.7	5

8.9 µg/Nm^3 at the outlet of the FGD systems. The other runs showed better agreement. On the second run the inlet elemental Hg concentration was 16.8 µg/Nm^3 and the outlet was almost the same at 16.5 µg/Nm^3. The third run showed 19.0 µg/Nm^3 at the inlet and 11.4 µg/Nm^3. These comparisons suggest that, particularly for the first run, the elemental mercury concentrations measured at the ESP outlet (FGD inlet) in December 1998 were biased high. The reason for this apparent bias is not known.

Over the course of the long-term tests at Site 1, the total mercury concentrations measured by the semi-continuous analyzer described in Section 2 varied over an even wider range than did the manual method measurements, from 4 µg/Nm^3 to 36 µg/Nm^3. Similarly, the measured elemental mercury concentrations varied from less than 2 to 18 µg/Nm^3. The inlet mercury oxidation percentage indicated by the semi-continuous analyzer varied from 30 to 80%.

The flue gas total mercury concentrations and mercury oxidation percentages measured with the EPRI semi-continuous mercury analyzer were compared with flue gas composition data measured with the plant's CEM system. The strongest correlations were between total mercury content and flue gas SO_2 and NO_X concentrations. The flue gas total mercury content was observed to be inversely related to flue gas SO_2 concentration. This correlation is illustrated in Figure 3-8. The R^2 value for a linear least-squares fit of these data is 0.72, indicating that these two parameters are likely related.
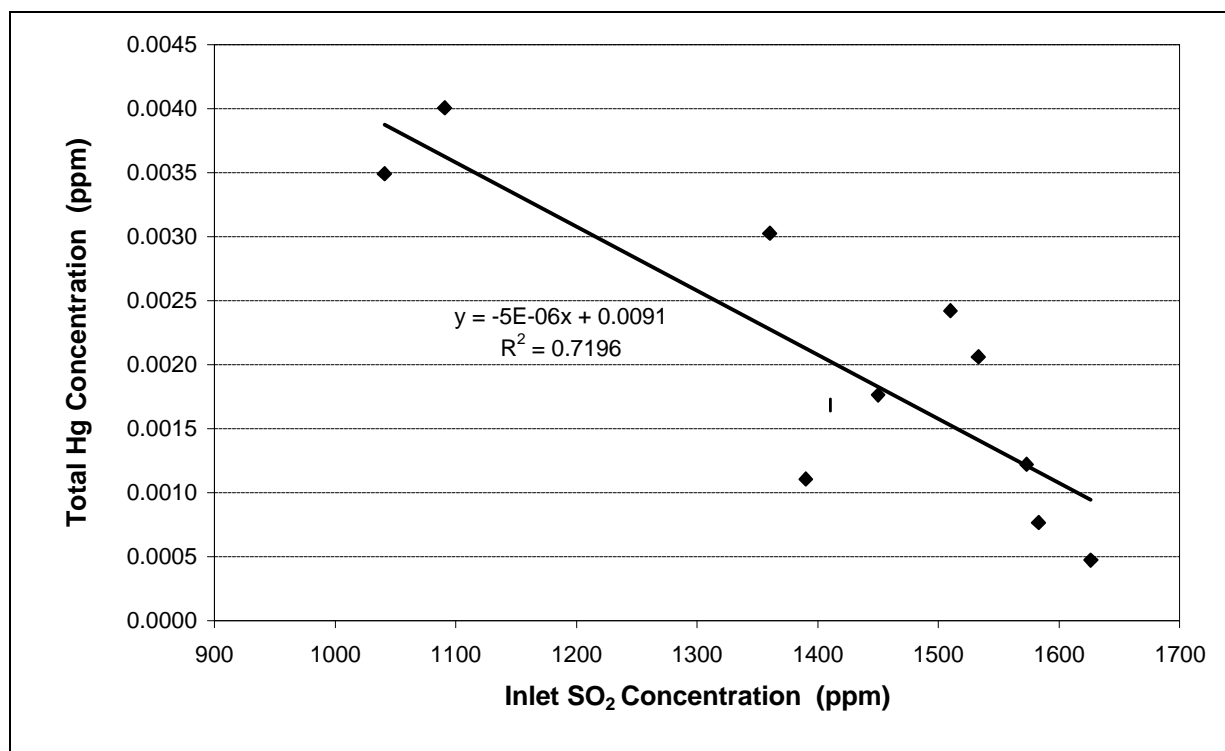
Figure 3-8
Total Mercury Concentration vs. FGD Inlet SO$_2$ Concentration at Site 1

The total mercury concentration data were observed to be related to flue gas NO_X concentration. These data are plotted in Figure 3-9. This is a weaker relationship than that with SO_2, with an R^2 value of 0.48. The material balance calculations summarized in Table 3-19 indicate that a high percentage of the coal mercury is accounted for in the gas phase of the flue gas at the ESP outlet. Thus, variations in flue gas mercury content appear to be directly related to changes in lignite mercury content and not affected by the distribution of mercury between the flue gas, bottom ash, and fly ash. These relationships suggest that for Site 1 the fuel mercury content is lower in lignite with higher sulfur levels and higher in lignite with higher fuel nitrogen content. However, it would take considerably more data to make this observation conclusive.
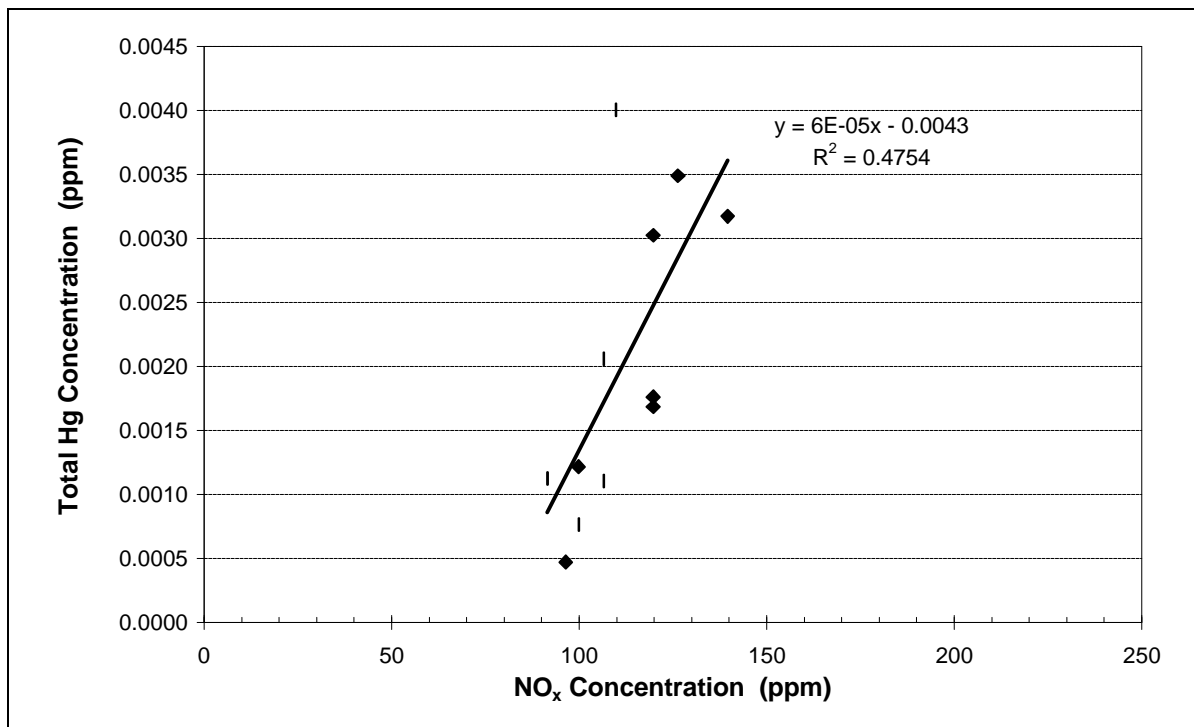
Figure 3-9
Total Hg Concentration vs. Flue Gas NO_X Concentration at Site 1

Other relationships were possibly identified, but the R^2 values for linear least squares fit of the data suggest that the relationships are weak at best (i.e., R^2 values of 0.3 or less). For example, mercury oxidation percentages appeared to increase with higher SO_2 and NO_X concentrations. Other parameters showed no obvious relationship with total mercury concentrations or oxidation percentages, such as boiler load and flue gas CO_2 concentrations (an indicator of excess air level). Data plots showing weak or no correlation are not included in this report.

Also during the test program at Site 1, the concentrations of trace metals in the flue gas were measured using Method 29. These results are presented later in this section, where trace metal results for all three sites are summarized and discussed.

Site 2

As described earlier in this section, flue gas mercury concentration measurements were made at Site 2 in December 1998, using the draft Ontario Hydro method. Simultaneous measurements were made in triplicate downstream of one of the unit's induced draft fans (FGD inlet) and downstream of one FGD module. The results showed an average total mercury concentration of 12.0 µg Hg/Nm^3 and an average gas phase elemental mercury concentration of 8.8 µg Hg/Nm^3 in the flue gas upstream of the FGD system. These values correspond to an average mercury oxidation percentage of 27% at the FGD inlet.

Samples of the coal fired at Site 2 were collected during each sampling run. The coal mercury content averaged 123 ppb (dry basis) in these three samples. Material balance calculations were conducted to compare the mercury in the coal fired versus that measured in the flue gas, and showed a very good average closure of 98%, with individual sample run closures of 65, 110, and 121%. This material balance is summarized in Table 3-21.

Table 3-21
Average Results of Mercury Balance Calculations for Site 2

Parameter	December 1998 Values
Coal mercury content, mg/kg	0.094
Amount of coal fired, tons/hr (100 kg/hr)*	197 (179)
Mercury in coal fired, lb/hr (g/hr)	0.0371 (16.8)
Total mercury concentration in ESP outlet flue gas, µg/Nm^3	12.0
Flue gas flow rate at ESP outlet, dscfm (Nm^3/s)*	855,000 (404)
Total mercury in flue gas, lb/hr (g/m)	0.0358 (16.2)
Mercury concentration in fly ash, mg/kg	0.020
Fly ash collection rate, tons/hr (1000 kg/hr)*	8.9 (8.1)
Mercury in fly ash collected, lb/hr (g/m)	0.0004 (0.2)
Mercury in bottom ash, lb/hr (g/m)	0 ([0]assumed)
Total mercury accounted for in flue gas and fly ash, lb/hr (g/m)	0.0362 (16.4)
Mercury material balance closure, % of coal mercury accounted for	98

*   By combustion calculation.

The flue gas sample runs at the FGD outlet location indicated an average total mercury concentration of 9.3 µg Hg/Nm^3 and an average gas phase elemental mercury concentration of 9.0 µg Hg/Nm^3. As expected based on results from other sites, the FGD system at Site 2 was observed to remove a high percentage (93%) of the oxidized mercury in the flue gas at the FGD

inlet, and essentially none of the elemental mercury. The overall mercury removal across the FGD system averaged 23%.

There was only one problem during the sampling runs that resulted in a concern about data quality. The sampling train failed its post-run leak check after the first run at the FGD inlet location. At first it was thought that the leak developed when the sampling probe was removed from the duct at the end of the run. However, higher flue gas oxygen content and lower flue gas mercury concentrations measured for this run compared to those of the other two runs at this location suggest that the leak occurred while the sample was being collected. The first run also showed the poorest closure in the coal mercury material balance calculations mentioned above (65%).

Subsequent flue gas analyses were conducted in March, 1999. At this later date, Method 29T showed similar total mercury concentrations at the FGD inlet averaging about 13 μg/Nm^3, and elemental mercury concentrations averaging about 8 μg/Nm^3. Method 29T sampling was not conducted at the FGD outlet location.

Also in March 1999, Method 29 was run at the FGD inlet location to measure the concentrations of trace species in the flue gas (other than mercury, mostly associated with the small amount of fly ash remaining in the ESP outlet gas). The total mercury concentration measured by Method 29 in three runs averaged 13.1 μg/Nm^3, which shows excellent agreement with the average results measured by the draft Ontario Hydro method in December 1998 and by Method 29T in March 1999. The average measurements by the three methods during the two time periods agreed within 9%.

The average concentrations of other metals measured by Method 29 at Site 2 are summarized later in this section, where the Method 29 results from all three sites are compared.

Site 3

Flue gas characterization measurements were made at Site 3 at the beginning of the long-term catalyst test, in mid-July 2000, and at the end, during the last two weeks of January 2001. The July measurements included measurement of speciated mercury concentrations by the draft Ontario Hydro method, mercury and total metals by Method 29, flue gas HCl, chlorine and HF concentrations by Method 26a, and sulfuric acid concentrations by the CCS method. Coal and fly ash samples were also collected during the flue gas testing.

Because test results with the field mercury analyzer used in concert with the long-term catalyst test indicated an appreciable drop in elemental mercury content in the FGD inlet gas since the beginning of the long-term test in July, it was decided to conduct more gas characterization tests. These gas characterization tests, conducted in January 2001, included total mercury and mercury speciation by the draft Ontario Hydro method, at FGD inlet and outlet locations and at the Site 3 air heater inlet and outlet. Figures 3-10 and 3-11 illustrate all of the sampling locations. The sampling at the air heater outlet location was conducted with the plant's ammonia injection system turned off, as the presence of ammonia in the flue gas would interfere with the measurement method. While measuring at the FGD inlet location with the ammonia injection
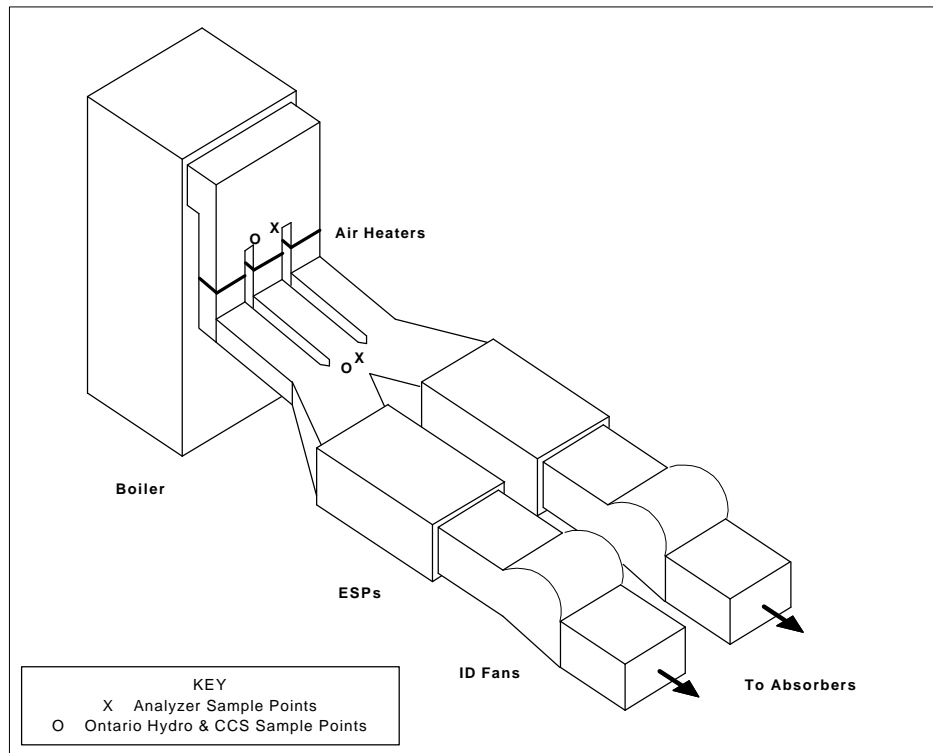
Figure 3-10
Sample Locations Located Upstream of the ID Fans
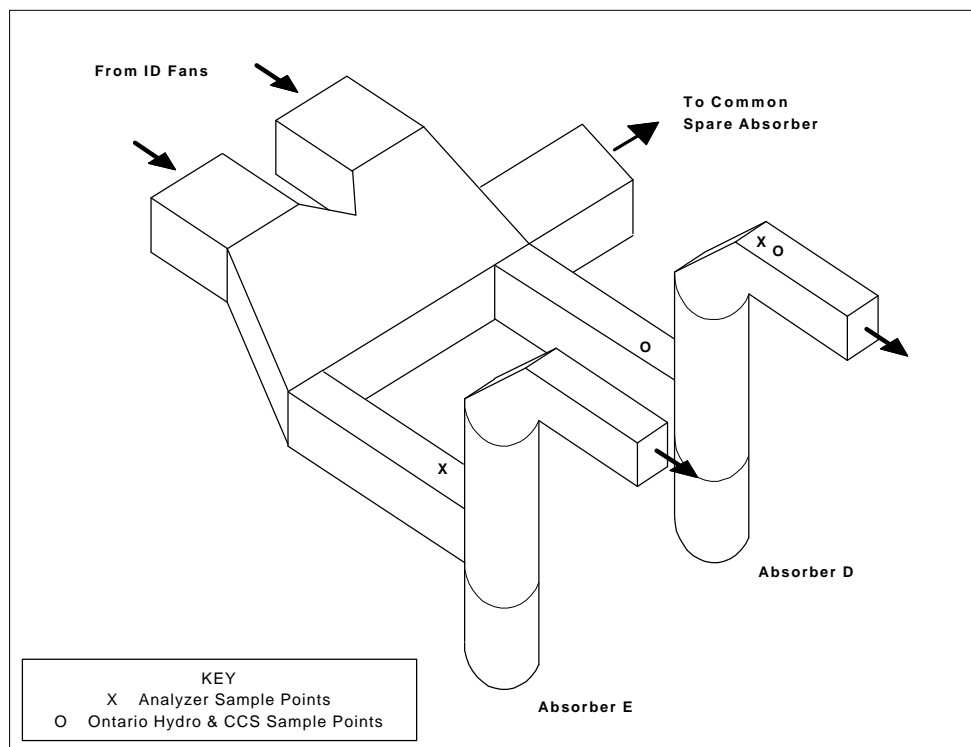
Figure 3-11
Sample Locations Located Downstream of the ID Fans

system in normal operation, ammonia slip measurements were also conducted. Coal and fly ash samples were also collected intermittently during flue gas testing.

Also in January, flue gas sulfuric acid concentrations were measured at all four locations mentioned above, using the CCS method. The air heater inlet and outlet locations were sampled simultaneously on one day, and the FGD inlet and outlet locations were sampled simultaneously on another day. As were the Ontario Hydro method measurements, the CCS measurements were made with the plant ammonia conditioning system turned off, but the FGD inlet and outlet measurements were made with the ammonia conditioning system in normal operation.

During the January 2001 effort, a second semi-continuous mercury analyzer was set up at Site 3, to allow simultaneous measurement of mercury concentrations and speciation at the FGD inlet and outlet locations.

The following presents and discusses the flue gas characterization data from Site 3, collected during July 2000 and January 2001.

Flue Gas Mercury Concentrations. Table 3-22 summarizes the July results from the Ontario Hydro method for total and speciated mercury concentrations in the flue gas at the FGD inlet and outlet. FGD inlet and outlet measurements were taken to compare the amount of elemental mercury in each stream. An apparent leak during the third sampling run at the FGD inlet prevented those results from being used.

Table 3-22
Results of Ontario Hydro Mercury Measurements at Site 3, July 2000

Sample	Oxidized Mercury (μg/Nm^3)	Elemental Mercury (μg/Nm^3)	Total Mercury (μg/Nm^3)	Mercury Oxidation (%)
Inlet-1	9.2	2.5	11.8	78
Inlet-2	9.6	4.3	13.9	69
Inlet-3*	6.0	0.2	6.1	97
Average	9.4	3.4	12.8	74
Outlet-1	0.58	0.56	1.14	51
Outlet-2	0.71	0.21	0.92	77
Outlet-3	0.24	0.19	0.43	55
Average	0.51	0.32	0.83	61

* Apparent leak during sampling, not included in average.

The results from the first two runs at the FGD inlet showed total mercury concentrations of about 13 μg/Nm^3. The mercury oxidation averaged about 74%, producing elemental mercury concentrations of about 3.4 μg/Nm^3. These concentrations and oxidation percentage are

consistent with measurements made in June and July 2000 with the EPRI semi-continuous field mercury analyzer at this location.

The results in Table 3-22 also indicate 95% removal of oxidized mercury across the FGD absorber, and over 90% removal of elemental mercury. The oxidized mercury removal percentage is consistent with results from other sites, but the high elemental mercury removal percentage is unexpected. Experience at the other two sites in this project and results from the EPA mercury ICR for systems with wet FGD led us to expect no removal of elemental mercury across the FGD system; an outlet elemental mercury concentration of 3 to 4 $\mu g/Nm^3$ was therefore expected. It is possible that the high apparent removal is due to an analytical problem with the outlet impinger solutions, leading to low recovery of mercury in the downstream (elemental mercury) impingers. However, no specific analytical problem was identified that explains this result.

Table 3-23 shows the results of the EPA Method 29 total mercury concentrations at the FGD inlet location. Method 29 sampling was not conducted at the FGD outlet location. Method 29 results represent a sum of recovered mercury from several sample train impingers and a probe rinse, and indicate only a total (not speciated) mercury concentration. Runs 2 and 3 show concentrations of about 13 to 14 $\mu g/Nm^3$ that are very similar to the total mercury concentrations in the first two Ontario Hydro runs. A much higher concentration of 21 $\mu g/Nm^3$ was indicated for Run 1, but even this higher value was in the range of individual measurements previously made with the EPRI semi-continuous field mercury analyzer at this location.

Table 3-23
Method 29 Mercury Results for the Site 3 FGD Inlet Location, July 2000

Run Number	Total Mercury Concentration ($\mu g/Nm^3$)
1	21.0
2	13.9
3	13.9
Average	16.3

Ontario Hydro method measurements were conducted again at the end of the long-term sand-bed reactor test at Site 3, in January 2001. FGD inlet and outlet Ontario Hydro results were conducted while the ammonia conditioning system was in service at the ESP inlet. Ammonia slip measurements were also made during the sampling effort; these results are not presented, as the measured values at the FGD inlet were all less than 0.2 ppm (the method detection limit). Ontario Hydro measurements were also made at the Site 3 air heater inlet and outlet. These measurements were made with the ammonia conditioning system out of service, as it was expected that the presence of ammonia in the sample gas would interfere with the Ontario Hydro method. The results of the Ontario Hydro measurements in January 2001 are summarized in Table 3-24.

Table 3-24
Ontario Hydro Method Results from Site 3, January 2001

Date/Time	Location	Elemental Hg (ug/Nm^3)	Oxidized Hg (ug/Nm^3)	Total Hg (ug/Nm^3)	Measured Hg Oxidation (%)
1/26/01 13:30	AH Inlet	7.1	37.1	44.2	84.0
1/26/01 15:30	AH Inlet	4.5	30.6	35.1	87.2
1/26/01 19:30	AH Inlet	5.1	28.7	33.8	84.8
Average		5.6	32.1	37.7	85.2
1/26/01 14:00	AH Outlet	9.9	27.3	37.2	73.4
1/26/01 16:00	AH Outlet	7.5	18.6	26.1	71.3
1/26/01 19:30	AH Outlet	12.7	15.3	28.0	54.6
Average		10.0	20.4	30.4	67.0
1/24/01 18:20	FGD Inlet	3.3	5.0	8.3	60.0
1/24/01 20:30	FGD Inlet	3.4	4.2	7.6	55.4
Average		3.4	4.6	8.0	57.8
1/24/01 17:30	FGD Outlet	3.95	0.6	4.6	13.4
1/24/01 20:00	FGD Outlet	5.03	0.6	5.6	9.9
Average		4.5	0.6	5.1	11.5

The results in Table 3-24 for the Ontario Hydro method testing at the FGD inlet and outlet locations show much higher elemental mercury concentrations than were measured with the field analyzer at either location. An average of 3.4 µg/Nm^3 was measured at the FGD inlet and 4.5 µg/Nm^3 at the FGD outlet, while the mercury field analyzer typically measured less than 1 µg/Nm^3 at the FGD inlet location and a second analyzer measured less than 3 µg/Nm^3 at the FGD outlet. There is no ready explanation for this discrepancy. The low elemental mercury concentrations were measured with two separate analyzers at the two locations. As discussed above, in July 2000, the field analyzer at the FGD inlet location was observed to be in good agreement with Ontario Hydro measurements. As described earlier in this section, a number of quality control measures were implemented on the field analyzer at the FGD inlet location in January, and no problems were identified.

The Ontario Hydro results from January show about 87% removal of oxidized mercury across the FGD system, but also a small increase in elemental mercury concentration across the FGD system. Both of these results are consistent with Ontario Hydro method data collected at other coal-fired sites equipped with wet FGD systems. However, we expected higher oxidized mercury removal percentages at this site, because the FGD absorber operates at a high liquid-to-gas ratio

of about 125 gpm/kacfm, and was designed to operate at 95% SO_2 removal efficiency. Furthermore, the removal of oxidized mercury measured across the FGD absorber at Site 3 by the Ontario Hydro method in July was higher than the January result, at 95%. However, the July results also showed 90% removal of elemental mercury across the absorber, which was not expected, while the January data showed a more expected small increase in elemental mercury concentration across the absorber.

There are several things to note about the air heater inlet and outlet results summarized in Table 3-24. First, the Ontario Hydro method results show the relatively high flue gas mercury concentrations expected based on the EPA mercury ICR coal data for this site. The ICR data showed that the Site 3 coal averaged about 0.25 ppm total mercury content, with some coal samples containing as much as 0.50 ppm. Based on the coal data, we expected to routinely see flue gas total mercury concentrations of 25 $\mu g/Nm^3$ and greater, but normally saw average values of only 10 to 15 $\mu g/Nm^3$ at the FGD inlet location. The results in Table 3-24 show that flue gas mercury concentrations are much higher at the air heater inlet location, where the flue gas temperature is about 700^oF (371^oC). The concentrations decrease across the air heater and ESP as the flue gas temperature drops to 300^oF (149^oC) and residence time is available for mercury adsorption on fly ash. The apparent mercury adsorption across the air heater amounts to about 19% of the inlet mercury, and that across the ESP and air heater together (i.e., at the FGD inlet) amounts to as much as 79% of the air heater inlet value. However, the FGD inlet sampling was done on a previous day, and the coal mercury content on that day was measured to be slightly lower. Given the small differences in coal sample mercury content for the two days, the apparent removal percentage of 70% may be overstated by one or two percentage points.

It is not clear what, if any, role ammonia might play in the adsorption of mercury on the fly ash. The mercury concentrations in the air heater inlet and outlet were measured with the ammonia injection system turned off, while the FGD inlet and outlet values were measured with the ammonia injection system operating. The effects of ammonia injection could, in part, account for the significant observed mercury removal across the ESP (approximately 60% of the air heater inlet mercury concentration). Fly ash samples collected during ammonia injection and subsequently while the ammonia injection system was turned off suggest a possible significant effect (see further discussions below).

Another thing to note about these data is that the elemental mercury concentration in the flue gas appears to increase across the air heater. This is not an expected result. The concentration of elemental mercury would be expected to decrease across the air heater due to two effects: 1) adsorption on fly ash, and 2) oxidation on fly ash surfaces and/or through gas phase reactions with HCl. We do not have a ready explanation for this result; it may represent sampling and/or analytical bias.

Overall, from the air heater inlet to the FGD system outlet, the data in Table 3-24 indicate 86% mercury removal, assuming that virtually all of the mercury in the coal is in the flue gas at the air heater inlet location. These Ontario Hydro speciation data show 98% removal of oxidized mercury from the air heater inlet to the FGD outlet, but only 20% removal of elemental mercury. These percentages underscore the potential effectiveness of a mercury oxidation catalyst installed at the FGD inlet location in improving overall mercury capture.

Other Metals in the Flue Gas. During the July 2000 gas characterization effort at Site 3, Method 29 was employed to measure the concentrations of other metals (besides mercury) in the flue gas at the FGD inlet location. As a result of there being a relatively high ash content in the flue gas downstream of the ESP at Site 3, the EPA Method 29 sampling results for other metals are being reported as solid phase metals and gas phase metals. Solid phase metals include the ash collected on the sample train filters and the probe nozzle rinse, while gas phase metals are those collected in the impingers during the sampling runs. The results are shown below in Table 3-25, along with a comparison of the Method 29 gas-phase metal results from Sites 1 and 2.

The most notable result in Table 3-25 is that the measured gas-phase selenium concentration at Site 3 was considerably higher than that measured at Site 1, which was fired with a Texas lignite. Selenium was identified as being a potential contributor to catalyst deactivation at Site 1, but such a tie has not been made with the Site 3 results.

Halogens in the Flue Gas. In July 2000, gas characterization data were also collected at the FGD inlet location for Cl_2, HCl, and HF using the EPA Method 26A. These data are summarized in Table 3-26, and show an average of less than 1 ppm of chlorine in the flue gas, 79 ppm of HCl, and 11 ppm of HF. The coal samples from Site 3 were not analyzed for chlorine or fluorine content as part of this project. However, the EPA ICR data for Site 3 showed the coal to average about 0.15 wt % chlorine. The measured Cl_2 and HCl concentrations in the Site 3 flue gas are consistent with a coal with approximately 0.15 wt % chlorine content.

Flue Gas SO_3 Concentration. Flue gas SO_3 gas characterization data were collected using the CCS sampling method during both the July 2000 and January 2001 gas characterization efforts. The results of the July 2000 measurements are shown in Table 3-27 below.

There are several things to note about the results in Table 3-27. First, the FGD inlet SO_3 concentrations are lower than would typically be expected for a medium sulfur bituminous coal. For bituminous coals, we would typically expect somewhere between 0.5 and 1.5% of the coal sulfur to be converted from SO_2 to SO_3. Therefore we would have expected SO_3 concentrations in the range of approximately 7 to 20 ppm. The measured values are much lower at 2.7 to 3.0 ppm. An initial explanation for the lower values measured was proposed after these July results became available. Site 3 injects ammonia into the flue gas downstream of the air heater and upstream of the ESP, as a fly ash conditioning agent. The injected ammonia reacts with flue gas SO_3 to form ammonium bisulfate salts that are collected in the ESP. These salts are sticky, and improve ash cohesiveness and lower ash re-entrainment losses from the ESP. Thus, it was anticipated that the lower-than-expected SO_3 concentrations at the FGD inlet (ESP outlet) sampling location were because of SO_3 removal in the ESP as an ammonia salt. However, measurements conducted in January did not confirm this supposition (see below).

The last four results shown in the table represent samples collected at the FGD outlet location in July. Of the four, the first two represent samples collected by the standard controlled condensation method, using and 10-ft (3.0 m) sampling probe, and the last two represent samples collected with additional residence time added between the sampling probe and the thimble filter used to removal fly ash from the sample gas. The additional residence time was added because at

Table 3-25
Method 29 Metals Results for the FGD Inlet Location at Sites 1 through 3

Parameter	Site 1 Gas Phase Concentration (ppb)	Site 2 Gas Phase Concentration (ppb)	Site 3 Gas Phase Concentration (ppb)	Site 3 Solid Phase Concentration (ppb)*
Aluminum	20.24	10.22	78.29	7568
Antimony	0.17	0.07	0.14	0.24
Arsenic	ND	0.01	0.76	11.65
Barium	0.09	0.08	0.13	11.61
Beryllium	0.27	0.06	0.01	2.64
Cadmium	0.05	0.02	0.01	0.06
Calcium	40.98	15.70	18.91	989
Chromium	0.19	0.12	0.30	9.89
Cobalt	ND	0.02	0.05	1.26
Copper	0.48	0.56	0.12	5.06
Iron	9.08	8.62	18.78	3736
Lead	0.11	0.05	0.05	0.88
Magnesium	3.02	3.05	3.64	318
Manganese	0.49	2.24	1.70	6.36
Molybdenum	0.01	0.02	0.08	3.56
Nickel	0.41	0.17	0.85	8.94
Potassium	89.30	3.17	9.50	592
Selenium	26.79	2.94	45.30	7.75
Silver	0.01	0.01	0.03	0.02
Sodium	191.31	120.24	90.66	290
Strontium	0.09	0.04	0.20	24.76
Thallium	4.52	0.40	7.95	0.04
Titanium	0.64	0.16	1.84	269
Vanadium	0.06	0.00	0.10	12.80
Zinc	2.09	2.30	1.12	8.57

* Solid-phase results are expressed as an equivalent parts per billion in the flue gas on a molar basis.

Table 3-26
Method 26A Sampling Results for the Site 3 FGD Inlet Location

Sample ID	ppm HCl	ppm Cl$_2$	ppm HF
M-26A-1	67.8	0.75	10.9
M-26A-2	81.2	0.24	11.0
M-26A-3	88.4	1.07	10.0
Average	79.1	0.69	10.6

Table 3-27
Controlled Condensation System Sampling Results for Site 3, July 2000

Run	SO$_3$ Concentration (ppmv)
Inlet-1	2.7
Inlet-2	3.0
Outlet-1	0.61
Outlet-2	0.53
Outlet-Extended Residence Time-1	0.85
Outlet-Extended Residence Time-2	0.62

the FGD outlet location, all of the SO$_3$ in the sample gas is actually present in the form of a condensed sulfuric acid mist. The sample probe and thimble holder are heated to 550°F (288°C) to vaporize this mist before the sample gas passes through the thimble filter. The additional residence time was added during the last two runs to help ensure that the acid mist was completely vaporized, as any mist remaining when the sample gas passes through the thimble might be removed on the thimble surface. The two runs with additional residence times averaged slightly higher SO$_3$ concentrations than the two with the normal sampling apparatus (0.7 ppm vs. 0.6 ppm). With only two runs in each configuration, though, it is not clear whether this represents run to run variations or indicates improved SO$_3$ recovery with the extended residence time. The two runs with the standard method indicate 80% removal of sulfuric acid mist across the FGD absorber, while the two runs with the extended residence time indicate 74% removal.

In January 2000, flue gas sulfuric acid concentrations were measured again using the CCS method at the two locations mentioned above, and at the air heater inlet and outlet locations. The air heater inlet and outlet locations were sampled simultaneously on one day, and the FGD inlet and outlet locations were sampled simultaneously another day. As were the Ontario Hydro method measurements, the CCS measurements at the air heater inlet and outlet were made with the plant ammonia conditioning system turned off, while the FGD inlet and outlet measurements were made with the ammonia conditioning system in normal operation.

The results of the January CCS measurements are summarized in Table 3-28. The data show the air heater inlet SO_3 concentrations averaged about 12 to 13 ppm (dry basis). Based on the average SO_2 concentrations measured along with these samples, the SO_3 values represent slightly less than 0.7% conversion of SO_2 to SO_3 in the boiler and back pass, which is at the low end of conversion percentages for bituminous, pulverized coal fired boilers. The data also show a significant drop in flue gas SO_3 concentration across the air heater, from 12-13 ppm down to 2-4 ppm (dry basis).

There are two potential reasons for such a drop. One is acid condensation on cool air heater basket surfaces on the "cold" side of the air heater wheel. The estimated acid dew point of the air heater inlet flue gas was calculated to be 275^oF (135^oC). If the air heater basket surface temperatures on the cold side of the wheel were below 275^oF (135^oC), sulfuric acid would tend to condense on the basket surfaces. The sulfuric acid concentration measurements were made near the center of the wheel, halfway between the cold and hot sides of the wheel. However, it is possible that basket surfaces were still cool enough at that point to condense sulfuric acid. The other potential reason for a drop in sulfuric acid concentration across the air heater is adsorption of sulfuric acid onto fly ash particle surfaces as the gas temperature drops across the air heater. The adsorptive capacity of the fly ash for sulfuric acid is temperature dependent, and the temperature drop should lead to additional adsorption.

At the air heater inlet and outlet locations, two different sampling train configurations were used. One was the standard train, where a quartz-lined probe was inserted perpendicular to the gas stream to collect a representative gas sample. The other used a series of cyclones in-duct on the probe end to separate approximately 95% of the fly ash from the sample gas (the probe by itself removes about 90%), to reduce the amount of ash collected on the thimble in the CCS train. This should presumably reduce the amount of sulfuric acid adsorption on the ash layer and improve the recovery of sulfuric acid from the sample gas. The series cyclones were expected to reduce any tendencies for a low measurement bias in the presence of a full fly ash loading in the sample gas (i.e., sampling upstream of the ESP). However, in both cases, the series cyclone train showed lower concentrations than the standard train, which is opposite the expected effect.

For the air heater inlet location, the small difference between the two trains may just be due to incidental air inleakage. The SO_3, SO_2 and moisture concentrations for the series cyclone train are all 5 to 7% lower than the values from the standard train. This does not appear to be the case for the air heater outlet location, though. It may just be that at the air heater outlet the series cyclone trains happened to be inserted into a port where sulfuric acid concentrations in the flue gas were lower than at the port where the standard configuration was used.

The FGD inlet values (ESP outlet) measured are higher than those measured at the air heater outlet (ESP inlet) even with the standard probe. This is not expected. If anything, some sulfuric acid should be removed by adsorption on ash within the ESP. However, several factors may explain this apparent discrepancy. First, the air heater outlet and FGD inlet were sampled on different days. The average SO_2 concentration measured at the FGD inlet was higher than that measured at the air heater inlet, suggesting higher coal sulfur levels for the former measurement. Coal samples from the two days confirm this effect; the coal sulfur content on the day of the FGD inlet sampling was 2.84 wt %, while that for the day of the air heater outlet sampling was

Table 3-28
Results of CCS Measurements Made at Site 3 during January 2001

Location/Method Modification	Measured SO$_3$ Concentration (ppmv)	Average SO$_2$ Concentration (ppmv, dry)	Average Moisture Content (volume %)
Air Heater Inlet – no modifications	14.4		
	7.8		
	14.0		
	14.5		
	12.4		
Average	12.6	1890	7.4
Air Heater Inlet – series cyclones	14.7		
	12.3		
	11.9		
	8.8		
	10.8		
Average	11.7	1790	7.0
Air Heater Outlet – no modifications	5.9		
	3.5		
	3.6		
	3.2		
	3.8		
Average	4.0	1660	6.2
Air Heater Inlet – series cyclones	2.3		
	2.1		
	1.9		
	1.7		
	2.1		
Average	2.0	1640	6.8

Table 3-28
Results of CCS Measurements Made at Site 3 during January 2001 (continued)

FGD Inlet – no modifications	4.5		
	5.4		
	5.9		
	6.5		
	5.7		
Average	5.6	1740	6.3
FGD Outlet – 10-ft probe	3.6		
	4.0		
	4.0		
	4.4		
	4.0		
Average	4.0	100	13.1
FGD Outlet – 5-ft probe	3.4		
	3.6		
	3.7		
	4.3		
	3.9		
Average	3.8	99	12.6

only 2.21 wt %. Also, it is known that air heater outlet SO_3 concentrations are typically stratified due to the temperature variation of the air heater baskets across the flue gas duct, as mentioned above. It is possible that the ports selected for air heater outlet sampling saw a lower than average flue gas SO_3 concentration, such that after the flue gas was mixed going through the ESP and ID fan, a higher value, reflecting the actual average, would be measured at the FGD inlet.

The FGD inlet values measured in January were also higher than those that had been measured in July. This could partly be a coal sulfur effect; the average coal sulfur content in July was 2.6 wt %, while the coal sample from the day of the FGD inlet CCS runs showed 2.84 wt %.

Note that the air heater inlet concentrations were measured on a day when the plant's ammonia conditioning system was taken out of service, while the FGD inlet values were made with the

ammonia system in service. It was expected that the ammonia injection would lead to greatly reduced sulfuric acid concentrations downstream of the ESP, as the objective of ammonia injection is to precipitate ammonium sulfate or bisulfate salts to condition the fly ash for improved ESP performance. The expected decrease in SO_3 concentration across the ESP was not seen in these data, although the coal sulfur variation and potential sample gas stratification at the air heater inlet, as described above, confounded this observation.

At the FGD outlet, two different probe lengths were used for the measurements; both a 5-ft (1.5-m) and a 10-ft (3.0-m) probe length were used. At the FGD outlet location, all of the sulfuric acid in the sample gas is present as a condensed, sub-micron acid mist. To be measured by the CCS method, this mist must be evaporated before the sample gas gets to the heated thimble in the CCS train, as ash reactions with condensed droplets can cause a low bias in the measurement. The two probe lengths were used to provide evidence of whether a 5-ft (1.5-m) probe length is adequate to evaporate all of the acid mist; previous testing and droplet evaporation calculations showed that a 10-ft (3.0-m) length would be more than adequate. The results in Table 3-28 suggest that for this FGD system, the 5-ft (1.5-m) probe length was adequate. The small difference in measured values for the two probe lengths is not considered to be significant.

A comparison of the FGD inlet and outlet sulfuric acid concentrations, which were measured simultaneously, does not show as great a drop in concentration across the FGD absorber as was expected. The measurements in July showed lower concentrations at both locations (2.7 to 3.0 ppm at the inlet and 0.5 to 0.8 ppm at the outlet) and an average of approximately 74 to 80% sulfuric acid removal. The data in Table 3-28 indicate only about 30% removal of sulfuric acid across the FGD system. The higher FGD inlet SO_3 concentration in January may partly be a result of the higher than normal coal sulfur level that day, as mentioned above. However, there is no obvious explanation for the lower SO_3 removal in January. The average SO_2 concentration data for the FGD inlet and outlet locations show 94% SO_2 removal across that absorber, which is near the design level of 95% removal, so it appears to have been operating normally with respect to its effectiveness as a gas contactor.

Coal and Fly Ash Analyses. Coal and fly ash samples were also collected during the flue gas testing. Results from mercury analyses of these samples are listed in Table 3-29. These show fairly wide variations in mercury concentrations for both sample types. Fly ash samples obtained at the same time from different hoppers showed appreciable differences. Part of the difference may be related to sample homogeneity and difficulties associated with obtaining representative fly ash samples from the individual hoppers. Regardless, results indicate an appreciable adsorption of mercury on the fly ash. It is not currently known what factors determine the ability of fly ash to remove mercury from flue gas, although factors that appear important include flue gas temperature and composition, fly ash exposure time to flue gas, and fly ash LOI (carbon content).

The coal samples showed relatively high mercury concentrations of 0.2 ppm or greater. Most showed concentrations in the range of 0.38 to 0.55 ppm. These coal mercury concentrations would lead to an expectation of flue gas total mercury concentrations in the range of approximately 30 to 50 $\mu g/Nm^3$. This is consistent with the January Ontario Hydro total mercury concentration data from the air heater inlet location.

Table 3-29
Results of Mercury Analysis of Site 3 Coal and Fly Ash Samples

Sample Date	Mercury Concentration (ppm)		
	Coal	Mill Rejects	ESP ash
6/28/00	0.215	-	0.309
7/11/00	0.439	-	0.738[1]
7/11/00	-	-	0.470[2]
10/03/00	0.553	-	-
1/23/01	0.513	0.963	-
1/24/01	0.382	0.479	0.335
1/25/01	0.458	3.05	-
1/26/01	0.405	-	0.272[3]

[1] Hopper 12.
[2] Hopper 13.
[3] Sample collected while the ammonia injection system was not operating.

A second observation is that the ESP ash sample mercury concentrations are nearly as high as those in the original coal samples. Since the ash represents about 12 to 16% of the as-received coal, mercury adsorbed on these ash samples most likely represents 10 to 15% of the mercury in the coal. There was some speculation that ammonia injection might enhance mercury adsorption on the fly ash collected in the ESP. The mercury content of the fly ash samples from 1/24 (ammonia on) and 1/26 (ammonia off) show about a 20% reduction in ash mercury content when the ammonia injection system was shut down. After taking the mercury and ash contents of these two coal samples into account, the amount of mercury collected with the fly ash could have been reduced by almost 40%. This is a potentially significant effect.

A third observation is that the coal pulverizer rejects (presumably pyrites) are higher in mercury concentration than the overall coal samples; in one case, significantly higher. This suggests an enrichment of mercury with pyrites in the coal. However, the quantity of mill rejects is estimated to be relatively minor (less than 1% of the coal throughput) so this apparent enrichment should not greatly impact a mercury balance around the power plant.

Fly ash LOI concentrations were measured in an attempt to explain the relatively high mercury levels in the ash. These results are summarized in Table 3-30. The LOI values are relatively high (approximately 5 to 8%) and may account for the significant mercury adsorption that appears to occur.

The results of ultimate and proximate analyses of coal samples from June, July, and January 2001 are summarized in Table 3-31. The results show the June and July coal samples to be consistent in sulfur content, at about 2.6 wt % in the coal, producing about 4.2 to 4.3 lb/MM Btu

Table 3-30
Results of LOI Analyses on Fly Ash Samples from June and July 2000

Sample Type	Sample Date	Loss on Ignition (wt %)*
Fly Ash	6/28/00	7.2
Fly Ash	7/11/00	8.3
Fly Ash (2A9-16)	9/26/00	4.6
Fly Ash (2B9-16)	9/26/00	4.6
Fly Ash (2A9-16)	10/03/00	6.2
Fly Ash (2B9-16)	10/03/00	5.6
Fly Ash	11/14/00	6.9

*   Average of two analyses.

Table 3-31
Results of Ultimate Analyses of Coal Samples from Site 3 (all values as received basis)

Sample Date	Ultimate Analysis (wt. % as received)							Heat Content (Btu/lb)*
	Moisture	Carbon	Hydrogen	Nitrogen	Sulfur	Ash	Oxygen	
6/28/00	5.04	69.66	3.99	1.22	2.62	13.02	4.55	12,220
7/11/00	4.68	71.23	4.41	1.29	2.62	10.73	5.04	12,510
1/23/01	6.66	66.46	4.02	1.21	2.84	14.74	4.07	12,093
1/24/01	5.80	68.08	3.85	1.21	2.92	16.02	2.12	11,949
1/25/01	7.88	68.26	4.17	1.24	2.21	12.80	3.44	12,079
1/26/01	7.46	68.26	4.09	1.21	1.97	13.11	3.90	11,910

*   12,000 Btu/lb is equivalent to 25.3 k-joules/g.

of SO_2. The January results show a much wider range of coal quality. The sample from January 24 has the highest ash and sulfur content, and the lowest heat content of the six samples for which results are available. The sample from the next day, January 25, has 25% less sulfur and 20% less ash than the January 24 sample. This illustrates the relatively wide range of coal quality that was encountered that week in January, a situation that was reported to us by plant personnel at the time and that is supported by the plant coal logs for this time period.

The coal and ash analysis results were used in a combustion calculation to estimate coal, flue gas and fly ash rates, then compared with the previous fly ash and coal mercury concentration data collected at Site 3 to calculate mercury mass balance closures. The mass balance closures are

shown in Table 3-32. Note that the June and July coal and ash samples were collected during short-term catalyst tests; due to a miscommunication with the plant, coal and ash samples were not acquired for the flue gas characterization period in July. The mass balance closures shown for June and July in Table 3-32 are based on flue gas total mercury content measured by the EPRI field analyzer rather than by the Ontario Hydro Method or Method 29. For the coal and ash samples collected on January 24, there are corresponding Ontario Hydro method flue gas mercury concentrations at the ESP outlet/FGD inlet location. These values were, in turn, used for the mercury balance calculations for that date.

Table 3-32
Summary of Mercury Balance Calculations for Site 3, June 2000 through January 2001

	6/28/00	**7/11/00**	**1/24/01**	**1/26/01**
Coal Hg Content, ppm dry basis	0.22	0.44	0.38	0.41
Coal Fired, tons/hr (1000 kg/hr)	340 (309)	332 (302)	377 (343)	3.25 (296)
Hg in Coal Fired, lb/hr (g/hr)	0.14 (63)	0.28 (126)	0.29 (130)	0.26 (119)
Fly Ash Hg Content, ppm	0.31	0.60	0.34	-*
Fly Ash Production Rate, lb/hr (kg/hr)	71,000 (32,000)	57,000 (26,000)	97,000 (44,000)	-*
Hg in Fly Ash, lb/hr (g/hr)	0.02 (10)	0.03 (16)	0.03 (16)	-*
Hg in Bottom Ash, lb/hr, assumed (g/hr)	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)
Hg in Coal Mill Rejects, lb/hr (g/hr)	-	-	<0.01 (<1)	<0.01 (<1)
Hg in FGD Inlet Gas, μg/Nm^3	15.7	22.7	8.0	37.7*
Flue Gas Rate, 10^6 dscfm (Nm^3/s)	1.90 (898)	1.91 (903)	1.82 (860)	158 (747)*
Hg in FGD Inlet Flue Gas, lb/hr (g/hr)	0.11 (48)	0.15 (70)	0.06 (25)	0.21 (96)*
Hg in Flue Gas + Ash, lb/hr (g/hr)	0.13 (58)	0.19 (85)	0.09 (42)	0.21 (96)*
Hg Balance Closure, %	92	68	32	80*

*   Material balance calculated for air heater inlet location. Mercury in ash contribution not considered.

The mercury material balance closures in Table 3-32 show relatively good closure (92%) for the samples from June 28, but poorer closure (68%) for the samples from July 11. With the wide range of observed flue gas, coal, and ash mercury contents at Site 3, and the observation that flue gas total mercury concentrations can vary markedly throughout the day, it would be expected that tight material balance closures would be difficult to achieve at this site. That is, it would be difficult to collect coal and ash samples that are known to be representative of the flue gas at any one point during the day of collection. Coal and ash samples collected at one time during the day may not correlate well with the flue gas at the time inlet mercury concentrations are measured.

That is most likely the reason the mercury mass balance closure for July 11 is not closer to 100%.

The mercury balance data for January 24 show a very poor closure. The amount of mercury accounted for in the coal mill rejects, ESP outlet/FGD inlet flue gas, and in the fly ash collected in the ESP account for only 32% of the mercury in the coal fired in the Site 3 boiler. There are several potential reasons for this poor closure. Perhaps the best potential explanation is that the coal quality was known to be quite variable over this time period, much more so that during the June and July measurement periods. Presumably the coal quality variations also greatly impacted coal mercury content. The poor material balance closure could well be due to coal, ash and Ontario Hydro flue gas samples being collected at different times during the day, and thus not reflecting a common coal mercury content. Furthermore, the coal and ash sample are merely grab samples from a single location for each. With variable coal quality, and given the size of the boiler at Site 3 (>750 MW) it is likely that grab samples are poor representations of the average compositions of these large process streams at any one time.

The mercury balance for January 26 was conducted on a different basis than the other balances. For this balance, we have air heater inlet flue gas mercury concentration data, so the balance was calculated for that location rather than for the FGD inlet. For the balance at this location, we assumed there would not be an appreciable amount of mercury in the fly ash at this temperature (650°F [343°C]). Consequently, the balance compares only the coal mercury content to the air heater inlet flue gas mercury content, avoiding the complication of having to collect representative fly ash samples to account for mercury removal across the air heater and ESP. This mercury balance closes relatively well (within the value of ±20% that is typically regarded as good closure for trace metal balances around full-scale power plants), even disregarding any mercury that might already be adsorbed by the fly ash at this location. This improved closure when comparing only flue gas measurements and a grab coal sample analysis suggests that the poor closures for the balances on July 11 and January 24 are, in fact, due to difficulties in collecting coal, fly ash, and flue gas samples all representative of the same conditions.

<u>Continuous Monitoring for Flue Gas Mercury Content</u>. During the test period in late January and early February 2001, two semi-continuous mercury emissions monitors (SCEM units) were used at Site 3 to characterize the flue gas at four different locations: the air heater inlet, the air heater outlet/ESP inlet, the ESP outlet/FGD inlet and the FGD outlet. Measurements were made with the intent of characterizing the effect of temperature, particulate removal, and scrubbing on flue gas mercury concentration and speciation. Measurements were also conducted by the draft Ontario Hydro method to verify mercury concentrations/speciation throughout the process. Figures 3-10 and 3-11 show the sample locations for both the analyzer and Ontario Hydro methods. In both figures, an 'X' indicates a sample location for the mercury analyzer (SCEM unit), and an 'O' indicates a sample location for the Ontario Hydro method. Figure 3-10 depicts the process upstream of the ID Fans and Figure 3-11 depicts the process downstream of the ID Fans.

Figure 3-12 shows the mercury concentrations and speciation, as measured by the SCEM, at the air heater inlet and outlet locations. Based on the results of previous research, it was expected that the flue gas mercury concentration would decrease across the air heater. This is due to the
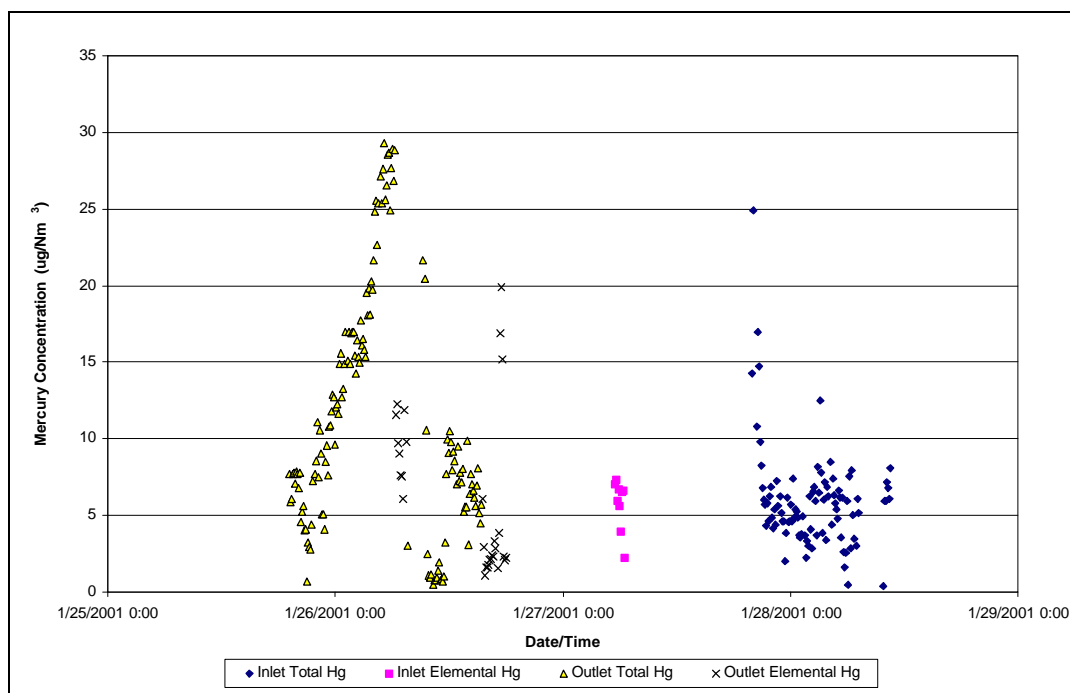
Figure 3-12
Mercury Concentration/Speciation at Air Heater Inlet and Outlet

mechanism for adsorption of mercury onto fly ash being more favorable at lower temperatures. Hence, decreasing the temperature of the gas from 650°F to 300°F (343 to 149°C) would be expected to result in greater mercury adsorption and lower flue gas mercury concentrations.

Based on Figure 3-12, it is difficult to tell the effect of the temperature decrease on mercury concentration. Changes in the coal fired and possibly combustion variations resulted in large fluctuations in mercury concentrations over this time period. These fluctuations made comparing measurements collected at different times difficult. Possible analytical problems further hindered the ability to compare mercury levels at the two locations. Mainly, analytical problems were apparent at the air heater outlet location, where continual shifts in the mercury levels were measured. Due to these variances, drawing a reliable conclusion as to the effect of decreased temperature on mercury levels was not possible based on SCEM results.

Figure 3-13 compares flue gas mercury concentrations and speciation across the ESP. Due to the ESP outlet location having a greater residence time during which mercury can be adsorbed by the fly ash, mercury levels would again be expected to be lower at the outlet location.

In Figure 3-13, the analytical problems at the ESP inlet (air heater outlet) are more apparent. While the mercury concentration at the ESP inlet varies greatly, measurements made simultaneously at the ESP outlet remain steady. Again, the uncertainty in the analytical results at the ESP inlet location makes comparing mercury levels at the two locations difficult.

Figure 3-14 compares mercury measurements made across the FGD system. Due to oxidized mercury being soluble in water, the majority of the oxidized mercury should be removed in the absorber, resulting in predominantly elemental mercury in the outlet gas.
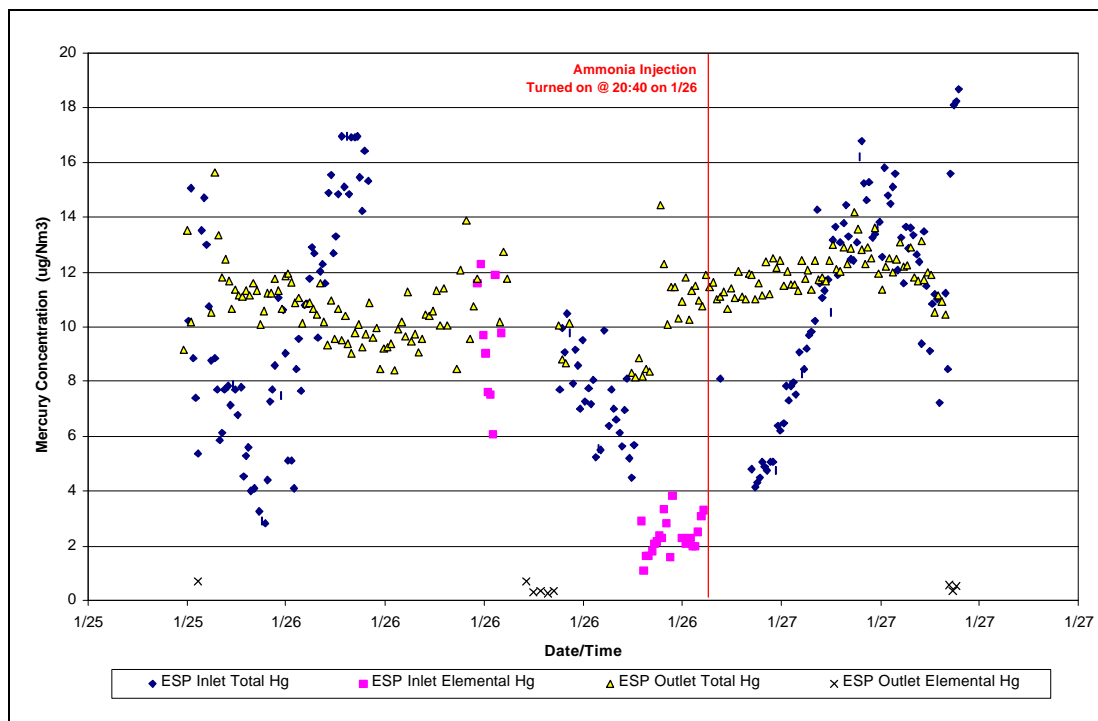
Figure 3-13
Mercury Concentration/Speciation ESP Inlet and Outlet
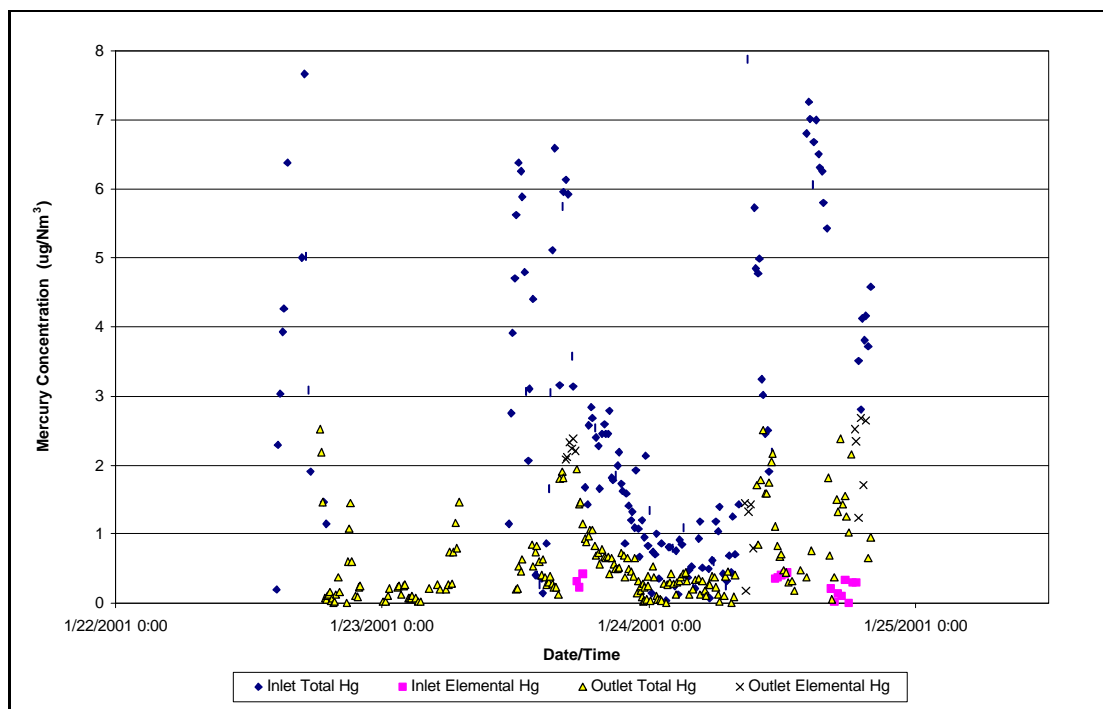
Figure 3-14
Mercury Concentration/Speciation at FGD Inlet and Outlet

As evident in Figure 3-14, there was a reduction in total mercury concentration across the FGD unit. Furthermore, the absorber outlet gas appears to be comprised of strictly elemental mercury. While there are huge variations in FGD inlet mercury concentrations, with values ranging from below 1 $\mu g/Nm^3$ to greater than 7 $\mu g/Nm^3$, the outlet concentrations tended to track with the inlet. Typically, the observed mercury removal across the FGD system in these SCEM results ranged from 50% to greater than 80%.

Process Correlations. During the testing in late January and early February, process data were collected to determine whether any process conditions correlated with flue gas mercury levels. The process data collected included: which coal was fired, unit load, total unit coal flow, boiler exit O_2 and carbon monoxide, FGD inlet SO_2 and opacity, stack NO_X and CO_2, economizer outlet temperature, air heater outlet temperature, and absorber inlet temperature. Of the process data collected over this time period, only the coal fired and opacity seemed to show any correlation with flue gas mercury concentrations.

As described earlier in this section, the measured coal sample mercury concentrations varied significantly during the one-week period over which mercury concentrations were measured in the flue gas. The highest coal sulfur content was over 30% greater than the lowest measured for the coal samples from that week. However, the flue gas mercury concentrations measured at the FGD inlet location varied by a much higher percentage, with the highest concentrations being an order of magnitude greater than the lowest. Also, the FGD inlet mercury concentrations, as measured by the mercury SCEM and by the Ontario Hydro method, were much lower than what was predicted based on the coal mercury concentrations. This is illustrated in Figure 3-15, which shows predicted concentrations in the range of 40 to 60 $\mu g/Nm^3$ while FGD inlet concentrations were measured to range from less than 1 to about 16 $\mu g/Nm^3$.

As described earlier in this section, the lower than predicted total mercury concentrations at the FGD inlet location have been attributed to mercury adsorption on the fly ash. What is evident from the data plotted in Figure 3-15 is that the percent of the mercury adsorbed on the fly ash varied markedly during the week. The apparent mercury removal percentages upstream of the FGD inlet location varied from about 75% on January 26 to greater than 90% during periods from the afternoon of January 23 through late on January 24.

Figure 3-15 also shows the approximate times that various coals were fired in the Site 3 boiler during the week. The coals included both low volatility (LV) and high volatility (HV) types that were either loaded into the Site 3 coal bunkers from trains, or were reclaimed off of the coal pile. Because the changes in coal fired were quite frequent over this period, it is difficult to attribute FGD inlet mercury concentrations to a given fuel. The time period shown for each coal is an estimate of when that coal was fired, taking into account the time each coal began loading into the bunkers and the approximate coal residence time in the bunkers. These estimates are only approximate, though, because effects such as "rat-holing" in the bunkers, differences in coal density and heat content, and variations in bunker inventories when a new coal was loaded would impact when the new coal started firing. Also, coal sloughing off of bunker walls could add a spike of the previous coal after a new coal had started firing.
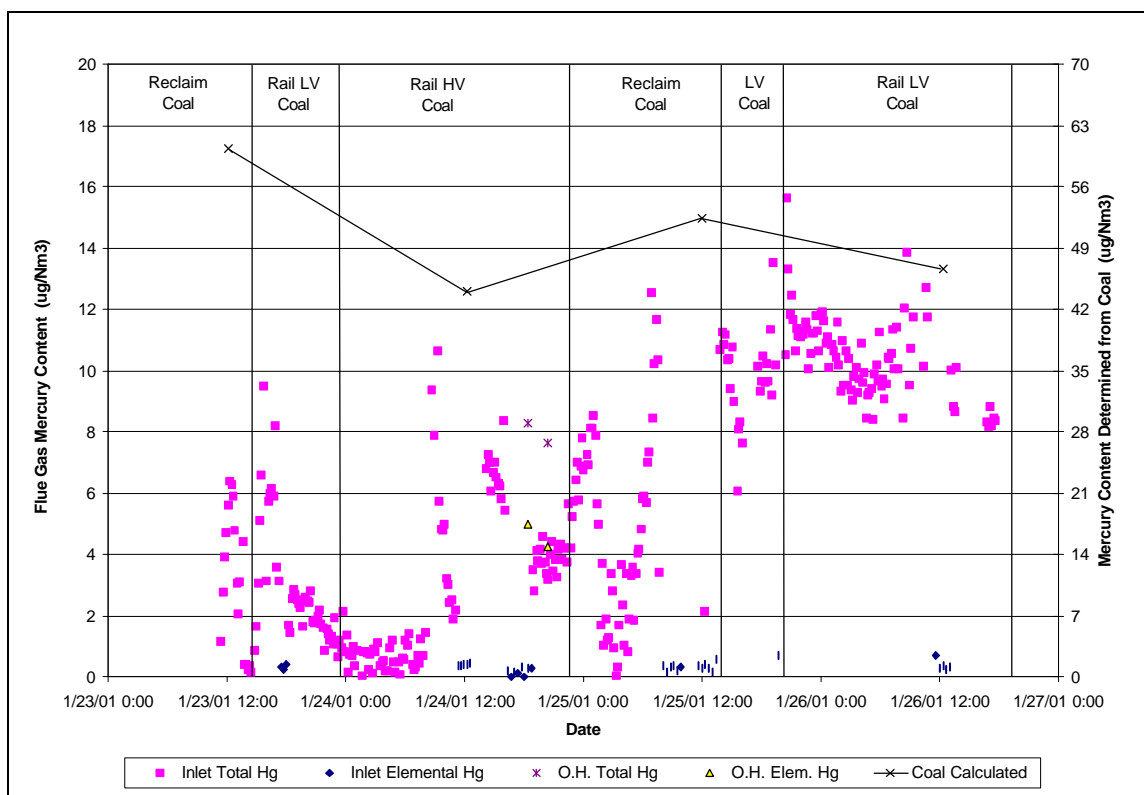
Figure 3-15
Relationship between Coal Mercury Content and Flue Gas Mercury Concentrations at the FGD Inlet

While it may not be possible to relate FGD inlet mercury concentrations or apparent mercury fly ash removal percentages to particular coals, the data in Figure 3-15 illustrate that the coals fired were being changed at approximately the same frequency that step changes in mercury concentration were being measured. Further indication that variations in coal type resulted in varying flue gas mercury concentrations is evident by the correlation between coal flow and mercury concentrations. Figure 3-16 plots the FGD inlet mercury concentration data along with coal flow and unit load. Whereas the unit load was relatively stable, the coal flow varied significantly over this time, which is an indication of the widely varying coal quality (e.g., variations in the as-fired coal heating value) during this time period. This plot lends greater credibility to speculations that coal quality variations caused the wide variations in measured FGD inlet total mercury concentrations.

Figure 3-17 is a plot of FGD inlet and outlet elemental mercury concentrations during the same time period as in Figure 3-16. The FGD outlet elemental mercury concentrations are considerably higher than at the inlet. The difference between the inlet and outlet elemental mercury concentrations is higher than would be expected based on the Ontario Hydro results. However, the two locations were not monitored for elemental mercury concentration at exactly the same times. Since the total (and presumably elemental) mercury concentrations were observed to vary markedly during this general time period, it is possible that the FGD outlet locations was measured for elemental mercury concentration during periods where the total
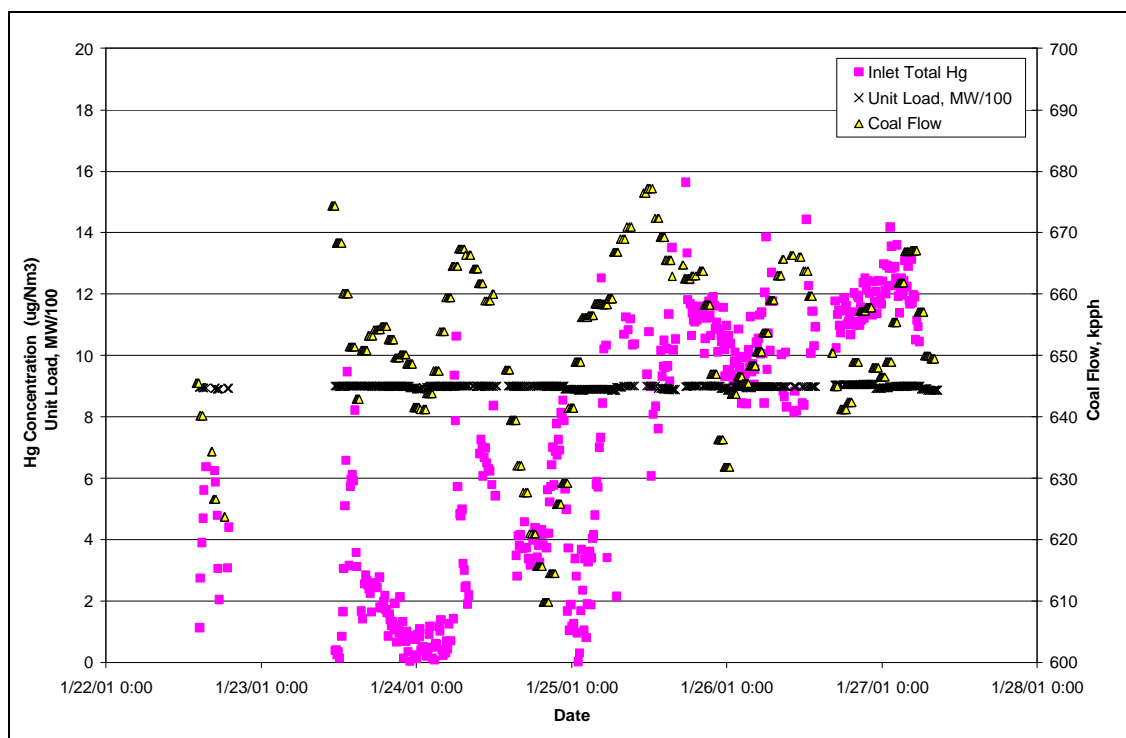
Figure 3-16
FGD Inlet Total Mercury by SCEM vs. Coal Flow and Unit Load
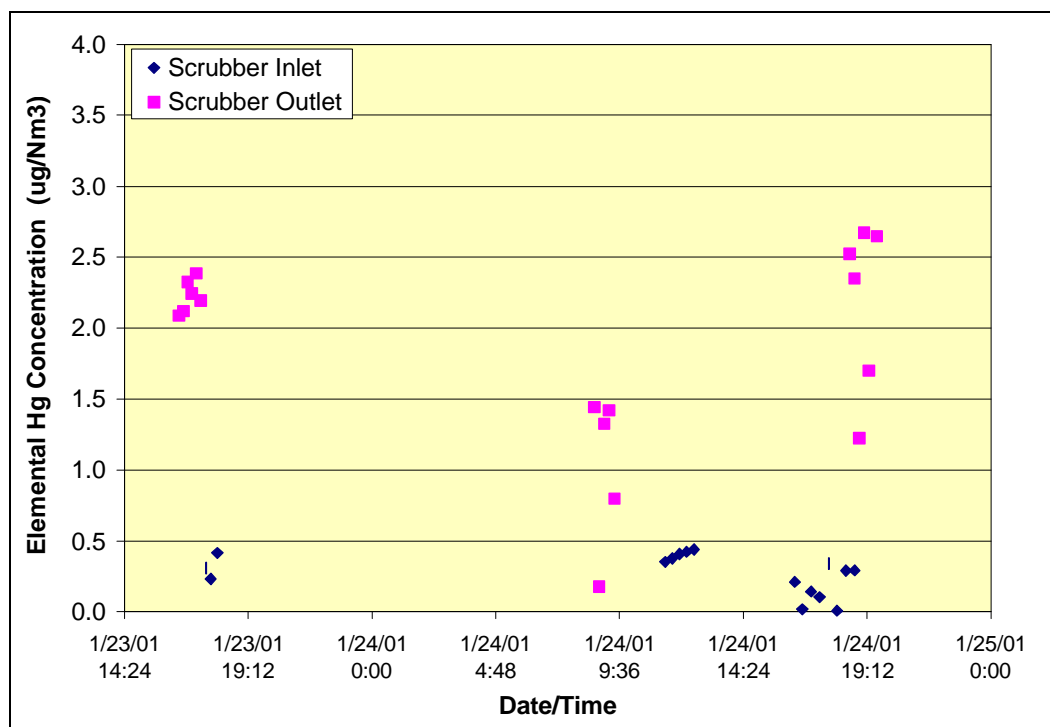
Figure 3-17
Results of Simultaneous FGD Inlet and Outlet Gas Monitoring for Total Mercury
Concentration by Mercury SCEM

mercury concentrations were higher than when the inlet elemental mercury was measured. Also, note that even at the FGD outlet location, the elemental mercury concentrations measured were considerably lower than were indicated by the Ontario Hydro method. It is apparent that some unknown effect was confounding either the SCEM or Ontario Hydro method results, or possibly both.

Since the coal fired was observed to have an effect on the flue gas mercury concentration, the remaining process data were only compared to flue gas mercury measurements made during time periods when the same coal type was fired. Based on the data, the only other correlation that could be found was the effect of opacity on flue gas mercury. Figure 3-18 shows the relationship between opacity, as measured at the FGD inlet, and flue gas mercury concentration.
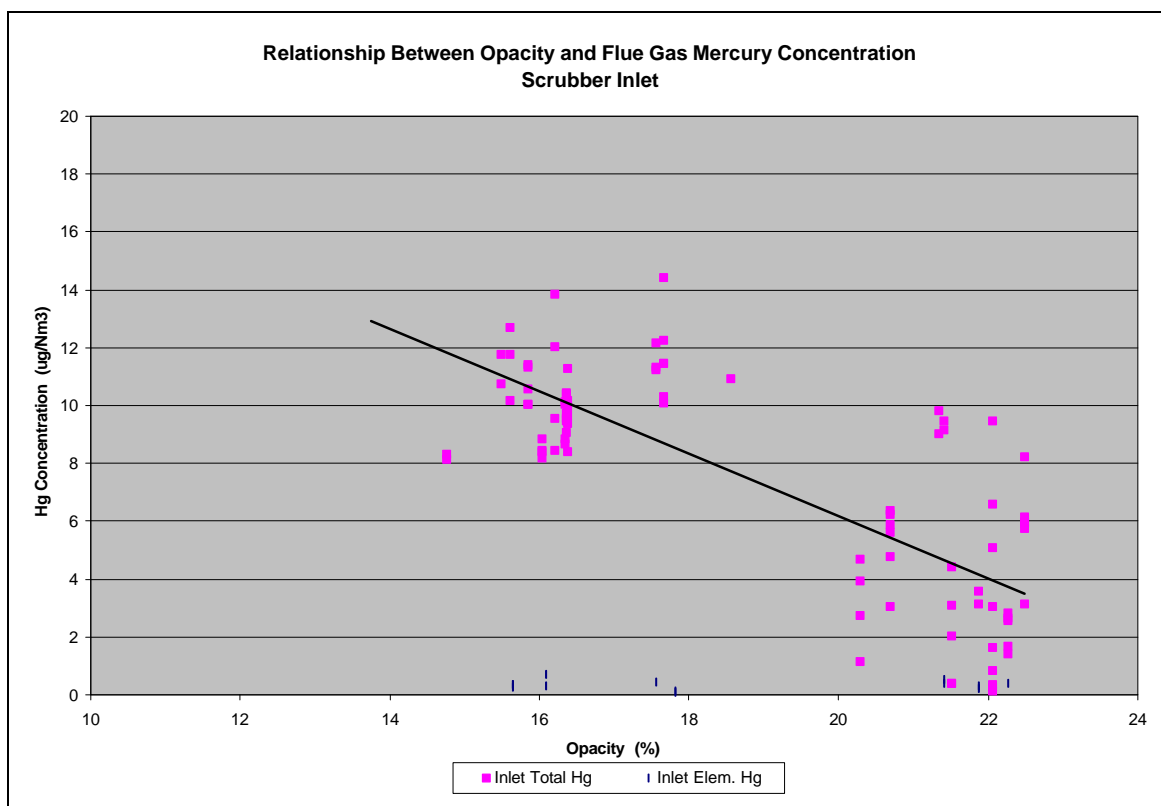
Figure 3-18
Relationship between Opacity and Flue Gas Mercury Concentrations at the FGD Inlet

As seen in the Figure 3-18, increased opacity seems to correspond to decreased flue gas mercury concentrations. There are two possible reasons for this phenomena: a change in combustion resulted in a higher LOI content of the fly ash, or a greater amount of fly ash provided more surface area for mercury adsorption to occur. Carbon is more difficult to remove in an ESP than fly ash due to its low resistivity, which can result in carbon being re-entrained into the flue gas after it is collected. The inability of the ESP to effectively remove the carbon content of a fly ash can result in increased opacity. Unburned carbon levels have been experimentally proven to correlate to mercury adsorption, with higher levels resulting in greater adsorption. Hence, higher LOI content typically results in lower flue gas mercury levels. A higher ash content coal could also result in increased opacity, as ESPs typically remove a relatively fixed percentage of the

inlet particulate. A greater amount of fly ash in the ESP inlet flue gas would provide more surface area for mercury adsorption to occur, and would tend to lower flue gas mercury content while increasing outlet opacity.

4
LABORATORY TEST RESULTS

Laboratory testing has been conducted throughout Phase II to support the field tests. Laboratory tests have been conducted primarily to screen catalysts for effectiveness at simulated flue gas conditions for each of the three sites, to attempt regeneration of catalysts recovered from the long-term sand bed reactor tests, and to determine what flue gas species may be responsible for catalyst deactivation. Each of these types of laboratory test efforts is discussed below.

A number of other ad hoc laboratory efforts have also been conducted as part of this project. Those efforts are discussed at the end of this section.

Catalyst Screening Tests

Prior to field testing, bench-scale tests were conducted to screen catalyst materials at simulated flue gas conditions similar to those expected at each test site. This allowed the field effort to focus on only the more active catalysts for a particular flue gas composition. The following section discusses the results of catalyst screening tests for each of the three sites.

Site 1 Screening Tests

Laboratory tests were carried out prior to field testing at Site 1 by reacting known masses of catalyst with a mercury-containing, simulated flue gas at 300^oF (149^oC). Table 4-1 lists the flue gas conditions tested, and compares those values to the actual values measured at Site 1. The simulated values were close to actual conditions.

In the laboratory screening tests, the effluent gas was monitored using the semi-continuous mercury analyzer to measure the concentration of total mercury exiting the column. Tests were run until adsorption equilibrium was reached. At this point the concentration of elemental mercury in the effluent gas was measured. Comparison of elemental and total mercury concentrations enabled the percent oxidation across the catalysts to be calculated.

Several tests were also conducted with two of the catalyst materials, Carbon #1 and Carbon#3, at "Baseline #5" conditions. The objective of these tests was to investigate the effect of NO_X concentration in the gas on the ability of the carbons to oxidize elemental mercury. Phase I tests with these samples had been conducted at similar conditions but without NO_X in the gas.

The concentrations of catalyst materials in the sand beds tested were selected based upon previous results with these materials. In general, carbon materials were tested at a loading of 20

Table 4-1
Simulated Flue Gas Conditions for Site 1 Laboratory Screening Tests

Parameter	Site 1 Simulation	Site 1 Measured Values	Baseline #5 Conditions
HCl (ppm)	1	1.0 – 1.8	50
SO_2 (ppm)	1400	1000 – 1500	1600
SO_3 (ppm)	0	0.7	0
CO_2 (%)	12	9.5 – 10.5*	12
H_2O (%)	8	Not measured	7
NO_X (ppm)	200	140 – 190	400
O_2 (%)	6	Not measured	6
Catalyst Temperature (^{o}F) [^{o}C]	300 [149]	300 [149]	275 [135]

* As measured at the stack; values at the FGD inlet were estimated to be about 1 percentage point higher.

mg in the sand bed while treating 1 L/min of simulated gas. Fly ashes and metal-based catalysts were tested at the same gas rate but a ten-fold higher, 200-mg loading in the sand bed.

The results of the bench-scale tests are listed in Table 4-2. Each carbon tested, with the exception of Carbon #5a, showed oxidation levels over 90%. Carbon #2 and Carbon #5 also showed high levels of mercury adsorption. Two fly ash samples (Bituminous Ash #3 and Subbituminous Ash #4) showed over 95% oxidization; lower oxidation levels were observed with the other ashes. The fly ash samples showed low adsorption capacities at these conditions.

The metal-containing catalysts showed differing results, with the palladium samples showing high oxidation percentages while the iron samples showed poor results. The Fe #1 catalyst and Fe #2 both showed much lower mercury oxidation than during Phase I tests. This suggests that some gas parameter, such as the lower HCl concentration than in the Phase I tests or the presence of NO_X, was responsible for inhibiting the iron catalysts. This further suggests that flue gas components have a large impact on the performance of the catalysts. The results for the iron-containing catalysts are consistent with the observed flue gas chemistry at Site 1. The Site 1 fly ash is rich in iron yet the mercury oxidation percentage was measured to be relatively low (i.e., the iron-rich fly ash is apparently not an effective in situ oxidation catalyst).

As noted above, several tests were performed under "Baseline #5" conditions to investigate the effect of higher NO_X concentrations on mercury oxidation. These tests indicated that the adsorption capacities of Carbon #1 and Carbon#3 decreased by a factor of two to four (from previous values of over 1200 µg/g) in the presence of 400 ppm NO_X. The oxidation percentages, however, were still very high. These results suggest that NO_X concentrations in the flue gas can have an adverse effect on carbon adsorption capacity, but may not affect oxidation activity.

Table 4-2
Results of Bench-Scale Oxidation Tests

Catalyst Type	Sorbent Mass in Sand Bed (mg)	Adsorbed Mercury (mg Hg/g sorbent)	Elemental Mercury Oxidation (%)
Site 1 Simulation Test Results			
Carbon #1	20	*	95
Carbon #1 repeat	20	201	100
Carbon #2	20	1780	96
Carbon #3	20	202	91
Carbon #5	20	1451	100
Carbon #5a	20	1084	17
Carbon #6a	20	143	97
Fe #1	200	6	7
Fe #3	200	78	23
Pd #1	200	12	91
Pd #3	200	12	98
Bituminous Ash #2b	200	2	49
Bituminous Ash #3	200	8	96
Subbituminous Ash #3	200	1	14
Subbituminous Ash #4	200	2	97
Subbituminous Ash #5	200	*	*
Subbituminous Ash #5	200	**	**
Baseline #5 Test Results			
Carbon #1	20	519	96
Carbon #1	20	620	No data
Carbon #3	20	348	95

* Operational problem prevented some or all pertinent data from being obtained.
** Test showed no mercury breakthrough after 2800 minutes; results were presumed suspect.

Table 4-3 compares the oxidation performance of the materials selected for screening in the field at Site 1 with the laboratory screening results presented above. In general, the laboratory and field data agree well. Notable exceptions are Carbon #5, Bituminous Ash #3, and Subbituminous Ash #4, which performed much better in the laboratory than in the field. There were no comparison data for Subbituminous Ash #5, for which the laboratory results were suspect.

Site 2 Screening Tests

Table 4-4 lists the gas compositions for the Site 2 simulation tests. Actual gas compositions that were subsequently measured at Site 2 are also shown in the table. In most instances the assumed values used for the simulation gas were very close to the actual flue gas values that were measured later.

Table 4-5 compares laboratory results to catalyst screening test results performed with the actual flue gas at Site 2. Oxidation measurements were made after the catalysts stopped adsorbing mercury. For most catalysts, the laboratory and field results were in close agreement. However, several catalysts performed better and some worse in actual flue gas than in lab tests. In particular, Carbon #2 and Carbon #6 did not perform as well in the field as in the laboratory, but Carbon #4 and Carbon #5 performed much better in the field than in the laboratory. These variations between field and laboratory results suggest that trace flue gas components not added to the simulation gas may affect the performance of some catalysts.

Site 3 Screening Tests

Table 4-6 lists the gas compositions for the Site 3 simulation tests, and actual gas compositions that were subsequently measured at Site 3. In most instances the assumed values used for the simulation gas were close to the values that were later measured for the actual flue gas. The exception was for elemental mercury, where the laboratory simulation gas contained more than the Site 3 flue gas to ensure that catalyst performance could be accurately measured.

Several carbon, ash, and metal catalyst materials were tested for oxidation activity in this simulated flue gas at 300°F (149°C). The results of these tests are summarized in Table 4-7. Results are also presented in the table for 275°F (135°C) and 325°F (163°C) gas temperatures. These are previous results from a separate EPRI project.

For some materials there are no results at a 300°F (149°C) gas temperature, which is the temperature at which the Site 3 field tests were conducted. However, it is probably safe to interpolate between the 275°F (135°C) and 325°F (163°C) temperature results for those materials.

With many of the carbons and ashes, a general trend of decreasing oxidation with increasing temperature was observed. The oxidation percentage for these samples at 300°F (149°C) often fell between those at the two other temperatures and the lowest oxidation percentages were generally measured at 325°F (163°C). For screening purposes, this trend supports the assumption that the oxidation level at 300°F (149°C) for samples with no data at that temperature can be interpolated from data obtained at the higher and lower temperature.

Table 4-3
Comparison of Field and Laboratory Catalyst Screening Test Results for Site 1

Catalyst Material	Hg^0 Oxidized by Catalyst	
	Site 1 Result (%)	Lab Result (%)*
Sand	8.2	-
Sand	3.3	3
Carbon #1, both beds	100	100
Carbon #1, one bed	100	100
Carbon #2, both beds	96.7	96
Carbon #2, one bed	100	96
Carbon #3, one bed	93.3	91
Carbon #4, both beds	94.6	No Data
Carbon #4, one bed	93.2	No Data
Carbon #5, both beds	62.2	100
Carbon #5, one bed	53.2	100
Carbon #6, both beds	98.9	97
Carbon #6, one bed	96.7	97
Pd #1, both beds	90.3	91
Pd #1, one bed	76.4	91
Pd #3, one bed	86.7	98
Bituminous Ash #2b, one bed	56.2	49
Bituminous Ash #3, both beds	61.1	96
Bituminous Ash #3, one bed	58.6	96
Subbituminous Ash #4, one bed	58.5	97
Subbituminous Ash #5	100	**
Subbituminous Ash #5	100	**

* Lab data are at an effective catalyst loading that is 33% greater than the loading one bed in the field test, 67% of the loading in two beds.

** No mercury breakthrough (complete adsorption) after 2800 minutes of testing; data are suspect.

Table 4-4
Simulated Flue Gas Compositions for Site 2 Simulation Tests

Flue Gas Parameter	Site 2 Simulation Gas	Measured Site 2 Gas Conditions
O_2 (%)	7	6 – 14
SO_2 (ppm)	200	250 – 350
SO_3 (ppm)	0	< 0.2
CO_2 (%)	13	11 – 13
HCl (ppm)	1*	1.1
NO_X (ppm)	200	130 – 200
H_2O (%)	10	12
Hg^0 ($\mu g/Nm^3$)	20 – 40	9 – 25
Temperature (°F) [°C]	300 [194]	300 [149]

* Some early tests were conducted with no HCl in the simulation gas.

Table 4-5
Comparison of Lab and Field Catalyst Screening Test Results for Site 2

	Elemental Mercury Oxidation Across Catalyst Bed, %	
Catalyst Type	Field	Laboratory
Sand	2	0
Carbon #1	78	77
Carbon #2	61*	80
Carbon #3	77	63
Carbon #4	89*	11
Carbon #5	50*	0
Carbon #6	82	100
Subbituminous Ash #5	80	70
Fe #1	29	8
Pd #1	90	90
Pd #3	92	95

* First fixed bed showed lower oxidation than the second (listed) indicating some deactivation.

Table 4-6
Simulated Flue Gas Compositions for Site 3 Simulation Tests

Flue Gas Parameter	Site 3 Simulation Gas	Measured Site 3 Gas Conditions
O_2 (%)	6	*
SO_2 (ppm)	1600	1530 – 1750
SO_3 (ppm)	0	2.7 – 5.6
CO_2 (%)	12	*
HCl (ppm)	50	79
NO_X (ppm)	200	*
H_2O (%)	7	6.2 – 6.8
Hg^0 ($\mu g/Nm^3$)	40 – 60	<1 – 7

* Not measured.

The results in Table 4-7 identified a number of materials that would be expected to result in approximately 80% oxidation of elemental mercury or greater in the field. Most of these materials were evaluated in short-term catalyst screening tests in the field at Site 3. Two of the active materials, Pd #2 and Pd #3, showed high elemental mercury oxidation percentages in the laboratory, but since these materials are similar in composition, performance, and presumably cost to the commercial Pd #1 catalyst, they were not tested in the field.

Table 4-8 compares the laboratory results from Table 4-7 with the results of the short-term catalyst screening tests at Site 3, as reported in Section 3. The carbons were generally less active in the field than in the simulation gas environment, particularly Carbon #4. Similarly, the fly ashes were all less active in the field than in the laboratory tests. Metal catalyst performance, though, was essentially the same in the field as in the laboratory for Fe #1 and Pd #1 materials, and the field result for the SCR catalyst actually showed better performance than in the simulation gas.

Table 4-9 lists the catalyst materials that performed markedly different in the field than in the laboratory (approximately 20 percentage points or greater difference) for all three of the test sites. For each site, the materials that performed better in the field than in the simulation gas are listed, then those that performed worse. Few consistent trends are seen in this list. Some carbons did better in the field than in the lab, while some did worse; most showed similar performance in the two environments. The fly ash materials generally performed more poorly in the field than in the laboratory. Note that Bituminous Ash #3 and Subbituminous Ash #4, which are on the "poorer performing" list for Sites 1 and 3, were not tested at Site 2.

Table 4-7
Laboratory Oxidation Test Results at Three Simulation Gas Temperatures

	Hg^0 Oxidation (%)		
	275°F (135°C)	300°F (149°C)	325°F (163°C)
Carbon Samples			
Carbon #1	94	98	95
Carbon #2	100	-	100
Carbon #3	95	-	95
Carbon #4	94	81	78
Carbon #5	21	-	16
Carbon #5a	94	-	87
Carbon #6	99	-	95
Fly Ash Samples			
Bituminous Ash #1	-	36	-
Bituminous Ash #2a	67	-	76
Bituminous Ash #3 – Phase I*	-	14	-
Bituminous Ash #3 – Phase II*	87	86	72
Subbituminous Ash #1	27	5	-
Subbituminous Ash #2	38	-	33
Subbituminous Ash #3	83	-	89
Subbituminous Ash #4	92	78	52
Subbituminous Ash #5	84	84	70
Lignite Ash #1	-	0	-
Lignite Ash #2	22	27	-
Oil-Fired Ash	-	4	-

Table 4-7
Laboratory Oxidation Test Results at Three Simulation Gas Temperatures (continued)

	Hg^0 Oxidation (%)		
	275°F (135°C)	300°F (149°C)	325°F (163°C)
Metal Catalyst Samples			
Alumina	-	0	-
Fe #1	-	88	-
Fe #2	-	50	-
Fe #3	-	95	-
Fe #5	-	83	-
Ni #1	-	0	-
Pd #1	-	92	-
Pd #2	-	95	-
Pd #3	-	96	-
SCR	-	57	-
Zn #1	-	0	-

* This is an apparent discrepancy between Phase I and Phase II naming conventions.

Catalyst Regeneration Tests

Bench-scale tests were also carried out to investigate the possibility of regenerating catalysts. Catalyst regeneration testing has been conducted on materials recovered from long-term testing at each of the three sites. These results are discussed below.

Regeneration of Samples from the First Long-term Test Period at Site 1

The recovered catalyst samples from Site 1 were first evaluated for mercury oxidation activity in laboratory oxidation tests with simulated flue gas. In these tests a portion (5 g) of the catalyst-sand mixture was placed in a 0.5-inch (13-mm) quartz tube and heated to 275°F (135°C). A mercury-containing flue gas, simulating that of Site 1, was then reacted with the catalysts. The gas exiting the fixed beds was analyzed for mercury. Tests were run until total mercury breakthrough was achieved across the column, such that no further mercury adsorption was occurring. The mercury exiting the bed was then speciated to evaluate the ability of the previously spent catalyst material to oxidize elemental mercury. The results of these tests are summarized in Table 4-10. The last column of the table shows the corresponding mercury oxidation results for these catalyst samples at the end of the first long-term test period at Site 1.

Table 4-8
Comparison of Laboratory Oxidation Test Results at 300°F (149°C) with Site 3 Short-term Screening Test Results

	Hg⁰ Oxidation (%)	
	Lab Result	**Field Result**
Carbon Samples		
Carbon #1	98	73
Carbon #2	100*	**
Carbon #3	95*	93
Carbon #4	81	7
Carbon #6	97*	62
Fly Ash Samples		
Subbituminous Ash #4	78	37
Subbituminous Ash #5	84	44
Bituminous Ash #3	86	-11
Metal Catalyst Samples		
Fe #1	88	90
Fe #5	83	**
Pd #1	92	92
SCR	57	87

* Interpolated from 275°F (135°C) and 325°F (163°C) results.
** Not measured because upstream bed in test apparatus maintained high activity for mercury oxidation over the duration of the short-term test.

Table 4-9
Comparison of Laboratory versus Field Performance Outliers at the Three Sites

Site 1 Results	Site 2 Results	Site 3 Results
Catalyst Materials that Performed Better in the Field than in the Laboratory		
None	Carbon #4	SCR
	Carbon #5	
	Fe #1	
Catalyst Materials that Performed Worse in the Field than in the Laboratory		
Carbon #5	Carbon #2	Carbon #1
Bituminous Ash #3		Carbon #4
Subbituminous Ash #4		Carbon #6
		Subbituminous Ash #4
		Subbituminous Ash #5
		Bituminous Ash #3

Table 4-10
Laboratory Results for Catalyst Materials Recovered from the Field Test Unit after 1100 Hours of Operation at Site 1

Catalyst Type (position in long-term test apparatus)	Catalyst Mass Reacted (mg)	Lab Mercury Adsorption Capacity ($\mu g/g$)	Lab Mercury Oxidation (%)	Site 1 Oxidation after 1100 hrs (%)
Subbituminous Ash #5 (1B)	100	639	99	0
Carbon #1 (2A)	16.7	40*	0*	0
Carbon #1 (2B)	16.7	660	97	26
Carbon #4 (3A)	16.7	1438	27	0
Carbon #6 (3B)	16.7	396	95	13
Pyrex Wool	1000	4	0	-
Sand (1A)	10000	0.16	0	-

* Average of two test results.

The results in Table 4-10 indicate that several samples showed much greater reactivity toward mercury in the simulated flue gas than they had when recovered from the field test unit at Site 1. The downstream Carbon #1 (position 2B in the field test unit) and Carbon #6 (position 3B) both showed mercury oxidation greater than 95%, as did the Subbituminous Ash #5 sample (position 1B). Each of these samples also showed high mercury adsorption capacities. The upstream Carbon #1 (position 2A) showed very little adsorption of mercury and no oxidation, indicating that it was indeed spent. The upstream Carbon #4 showed relatively low oxidation (27%) despite a high adsorption capacity.

The high activity of some catalysts in the bench tests suggests that they were not permanently deactivated after 1100 hours of flue gas operation. It is not obvious what caused the differences in activity between the field and bench tests. It is likely that changes occurred at the catalyst surfaces (e.g., species desorbed) after being removed from the Site 1 flue gas. The lab results appeared to indicate that a species present in the Site 1 flue gas is able to affect catalyst performance without permanently altering the catalyst surface. It is interesting that the three samples that showed high mercury oxidation in bench tests were all located in the second (downstream) fixed beds in the catalyst test unit. This suggests that they may have been shielded from harmful species by the upstream beds. The adsorption of such species could explain why the carbons located in upstream beds (Carbon #1 location 2A and Carbon #4) appear to have been affected more permanently.

During the long-term field tests, it was apparent that selenium was adsorbed to the surfaces within the reaction vessel. The Site 1 flue gas is known to contain relatively high selenium levels, as was shown in the Method 29 results in Section 3. This selenium content was evident by a pink color in the removed sand and pyrex wool packing. Bench-scale adsorption/oxidation tests were carried out with samples of the "pink" sand and wool to evaluate their activity toward mercury; reagent sand and wool normally show no activity toward mercury. These results are also included in Table 4-10.

Although neither sample oxidized mercury in the simulated flue gas, both showed the ability to adsorb mercury. The treated pyrex wool achieved over 90% mercury removal during the initial stages of the test, and a total adsorption capacity of 4 μg/g. The sand showed a much lower mercury capacity of 0.16 μg/g. Although this value is quite low, if similar adsorption on the sand occurred in the other Site 1 samples, the sand would have been responsible for a positive adsorption bias of approximately 60 μg/g in the carbon test results in Table 4-10.

These test results suggest that selenium and/or some other species adsorbed on the sand and pyrex wool and reacts with mercury. Another interesting observation was that selenium apparently desorbed from the catalyst surfaces during all of the bench-scale adsorption/oxidation tests with the materials recovered from Site 1. This was evident by color changes in the downstream sample lines as well as in some impinger solutions. These qualitative results indicated that the selenium could be easily removed from the catalysts.

Once the performance of the catalysts recovered from Site 1 in synthetic flue gas was determined, laboratory regeneration tests were conducted. These tests involved treating the spent catalysts with either CO_2 or N_2 gas at a given temperature for periods up to several hours. The

ability of the treated catalysts to oxidize elemental mercury in simulated flue gas was then evaluated.

Regeneration tests began by placing 5 g of the Site 1 spent catalyst/sand mixtures in a temperature-controlled column. After warming the column to the desired temperature, tests were started by flowing 1 L/min of a regeneration gas across the catalysts. The amount of mercury exiting each column was followed using the semi-continuous mercury analyzer. Each test was run until no mercury desorbed from the catalysts; test periods were generally 2 to 3 hours. Upon completing the regeneration tests, the temperature of each fixed-bed column was adjusted to 275°F (135°C). Mercury adsorption/oxidation tests were then performed by reacting each bed with a synthetic flue gas that simulated Site 1 conditions. The amount of mercury adsorbed by the catalysts was monitored. Upon reaching adsorption equilibrium, the mercury oxidation across each catalyst bed was then measured.

Regeneration and oxidation tests were carried out with Site 1 spent Carbon #1 (upstream bed) and Carbon #4. Both were recovered after the first long-term test period and both proved inactive in the bench-scale, simulated flue gas oxidation tests described above. Regeneration and oxidation tests were also carried out with Carbon #6 which, although inactive when removed at Site 1, showed a high level of activity (95% oxidation) in the subsequent lab tests with synthetic flue gas. The purpose of testing this catalyst was to ensure that the regeneration process did not have a detrimental effect on catalyst performance. All three samples were tested with CO_2 as the regeneration gas; this gas was chosen because it is known to be used in some carbon activation processes. Carbon #4 was also regenerated in nitrogen.

The results of the regeneration tests are compared in Table 4-11 to previous bench-scale and Site 1 results with these same catalysts. Improvements were obtained for each of the samples when treated at the higher regeneration temperatures (700°F to 800°F [371 to 430°C]). The two previously inactive catalysts (Carbon #1 and Carbon #4) oxidized over 90% of the elemental mercury after this regeneration. Regeneration tests performed with these two catalysts at the lower temperatures of 275°F (135°C) and 400°F (200°C) produced little improvement in catalytic oxidation. No significant difference was observed between nitrogen and carbon dioxide as the regeneration gas for Carbon #4.

As described above, mercury desorption occurred during each of the regeneration tests. The amount desorbed in the presence of CO_2 increased as the temperature was increased to 700°F (370°C) or 800°F (430°C). The amount of mercury desorbed from Carbon #4 in the presence of nitrogen at 700°F (370°C) was less than desorbed in CO_2 at the same temperature.

Adsorption of mercury by each regenerated catalyst was measured in the subsequent oxidation tests, which were conducted with simulated Site 1 flue gas. The extent of adsorption was greater for samples regenerated at higher temperatures and was typically higher than the amount desorbed. This suggests that the regeneration process involves reactions at the surface that change or remove species other than just mercury. One observation during the regeneration tests was the presence of red deposits at some locations in the sample lines or impingers downstream of the fixed bed; it is believed that these deposits were rich in selenium. This indicates that while

Table 4-11
Results of Bench-Scale Catalyst Regeneration Tests

| Catalyst Type | Regeneration Conditions | | Desorbed Hg (µg) | Re-adsorbed Hg (µg) | Elemental Hg Oxidation (%) | | |
	Gas	Temp. (°F) [°C]			Post-regeneration	Pre-regeneration (Lab)	Previous Site 1 Value
Carbon #1	CO_2	275 [135]	10.8	5.8	22	0	0
Carbon #1	CO_2	800 [430]	17.8	7.9	93	0	0
Carbon #6	CO_2	400 [200]	3.5	14.3	95	95	13
Carbon #6	CO_2	700 [370]	6.2	19.3	98	95	13
Carbon #4	CO_2	400 [200]	4.6	1.0	37	27	0
Carbon #4	CO_2	700 [370]	6.7	20.3	91	27	0
Carbon #4	N_2	700 [370]	3.3	35.2	93	27	0

selenium appeared to have enhanced mercury adsorption by the sand and pyrex wool, it may also play a role in inhibiting mercury catalytic oxidation.

The results of these regeneration tests were promising, and indicate that regeneration of the spent catalysts should be possible. It is not known, however, how the catalyst life of the regenerated materials will compare to that of the original, virgin materials over an extended period of operation in flue gas.

Regeneration of Catalysts Recovered from the Second Long-term Test at Site 1

Laboratory tests were also conducted on Site 1 catalysts recovered from the second long-term test, in simulated Site 1 gas, to determine their activity after they were removed from the long-term test apparatus. Performance tests were also conducted on fresh (reagent) catalyst materials at the same catalyst loading (catalyst concentration in sand) as used in the field samples, to allow for direct comparison of results with the recovered catalysts recovered. Results of the tests with both the fresh (reagent) and recovered catalyst materials are shown in Table 4-12 and Figure 4-1.

The results in Table 4-12 and Figure 4-1 show that the elemental mercury oxidation percentages for recovered field samples generally equaled or exceeded those of the virgin material, and were higher than were measured in the field at the end of the second long-term test at Site 1. Similar effects were seen in the materials recovered from the first long-term test period at Site 1. Although the samples were measured to be either partially or completely spent at the end of Site 1 long-term pilot tests, oxidation performance appears to have been restored in a similar gas but without any trace components such as selenium or sulfuric acid.

Table 4-12
Adsorption Capacity and Oxidation at Site 1 Simulated Conditions for Virgin Material and Recovered Field Catalyst Samples

Catalyst Type	Catalyst Loading (mg/g Sand)	Hg Adsorption Capacity (μg Hg^0/g Sample)		Elemental Hg Oxidation (% Inlet)		
		Fresh Material	Field Sample in Lab	Fresh Material	Field Sample in Lab	Field Sample at Site 1
Sand	1000	-	0	-	0	0
Carbon #1 – First Bed	6.7	490	73	81	95	89**
Carbon #1 – Second Bed	6.7	490	1300	81	97	0
Carbon #2	6.7	780	4580	97	98	76**
Subbituminous Ash #5	37.3	300	>2590*	32	65	0
Pd #1	40	5	130	83	70	0

* Estimated.
** These Site 1 field test values are suspect because of an apparent measurement bias at the end of the second long-term.
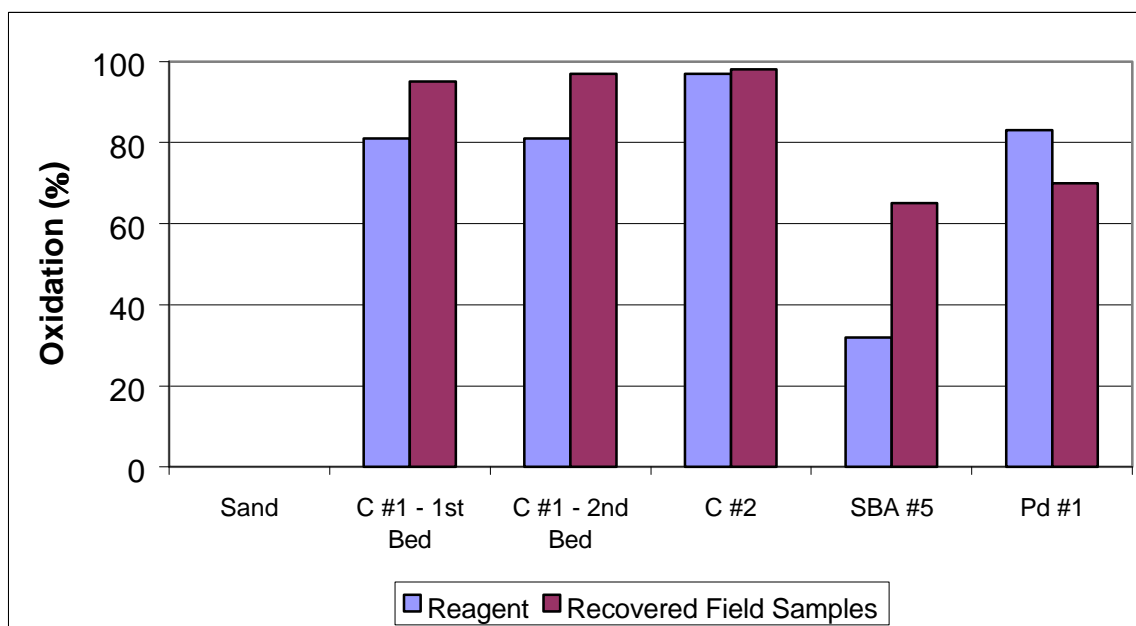
Figure 4-1
Comparison of Elemental Mercury Oxidation by Virgin Material and Recovered Field Samples at Simulated Site 1 Conditions

Because the recovered materials showed such high activity in the simulated Site 1 gas in the laboratory, catalyst regeneration tests were not conducted on these recovered materials per se. However, as described later in this section, these materials were exposed to regeneration gases and concentrations of the desorbing species were measured.

Regeneration of Catalysts from the Site 2 Long-term Test

Initial laboratory mercury adsorption and oxidation tests were carried out on the recovered catalyst samples to verify field results. Recovered samples were exposed to simulated flue gas at the conditions listed in Table 4-4. Mercury adsorption and oxidation were measured for each catalyst, as shown in Table 4-13. Recovered catalysts showed very low levels of mercury adsorption indicating that saturation had indeed occurred in the field test. The field sand "blank" was also tested and showed no mercury adsorption. Oxidation values in the field and lab corresponded within 14 percentage points, which is reasonable agreement considering the potential for measurement error at lower oxidation percentages (i.e., the percentage is based on the difference between two relatively large values). Carbon #3 remained virtually inactive, both beds of Carbon #6 showed some remaining activity, and both Pd #1 and Subbituminous Ash #5 continued to show high oxidation activity. The Site 2 sand blank showed no mercury oxidation in the laboratory test.

Table 4-13
Adsorption and Oxidation of Mercury by Recovered and Regenerated Catalysts from Site 2 Long-term Tests

Sample	Adsorption Capacity (µg Hg/g)		Elemental Mercury Oxidation (% of Inlet Hg^0)		
	Recovered Sample	Regenerated Sample	End of Field Test Sample	Recovered Sample	Regenerated Sample
Carbon #3	4	31	0	14	25
Carbon #6 – Bed 1	0	45	40	40	94
Carbon #6 – Bed 2	0	0	78	80	92
Subbituminous Ash #5	5	433	87	98	82
Pd #1	5	9	96	95	92

Next, tests were performed in which deactivated catalysts were purged with CO_2 at elevated temperature in an attempt to regenerate the samples. A 10-gram fixed bed of each recovered catalyst/sand mixture was heated to 700°F (370°C) then purged with CO_2 for 120 minutes. The "regenerated" samples were then tested in simulated flue gas to determine any effect on mercury adsorption capacity or oxidation. These results are also included in Table 4-13.

The results in Table 4-13 show that regeneration improved the performance of the deactivated carbon samples. Carbon #3 showed some improvement in adsorption capacity while mercury oxidation improved from zero to 25%. The adsorption capacity of the first bed of Carbon #6 showed improvement while the second bed still showed no adsorption. Both beds showed very high oxidation levels (>90%) after regeneration. These results suggest that the mechanisms of mercury adsorption and oxidation are not dependent upon each other for this sample. The two samples that showed good performance at the end of the Site 2 long-term test (Subbituminous Ash #5 and Pd #1) showed no improvement in mercury oxidation upon regeneration. However, Subbituminous Ash #5 showed a dramatic increase in adsorption capacity.

This regeneration testing has shown that most deactivated samples were easily regenerated in CO_2. The extent of regeneration varies some by catalyst type. The ability to regenerate the oxidation catalysts should have dramatic implications on the overall cost of this process (see Section 5).

It is interesting to note that many of the deactivated catalyst samples from the Site 1 testing were apparently regenerated by exposure to simulated flue gas that did not contain trace species such as selenium or sulfuric acid. In contrast, the deactivated catalyst samples from Site 2 remained inactive in the simulated gas. However, the inactive materials from both sites (as measured by performance in simulation gas) could readily be restored by exposure to CO_2 at elevated temperature.

Regeneration of Samples from the Long-term Test at Site 3

Catalyst materials from the long-term test at Site 3 were recovered from the field and tested in the laboratory to verify oxidation and adsorption capacities. In these tests, a portion of the recovered sample was placed in a fixed-bed configuration and reacted with simulated flue gas at 300ºF (149ºC). Table 4-14 displays the results of the laboratory tests on recovered catalysts compared to the November field test results. The latter represent the last oxidation performance data that were measured for the long-term test materials.

All of the recovered catalysts showed measurable adsorption capacity in the laboratory, while they had appeared to be at or near mercury adsorption equilibrium in the field. This indicates that some regeneration occurred after removing the catalysts from the Site 3 flue gas and exposing them to simulated flue gas. For Subbituminous Ash #5, the adsorption capacity was so great that after 24 hours of exposure to simulation gas, it was not possible to measure an oxidation percentage, as too high a percentage of the total mercury was still being adsorbed. This is similar to results observed with the original sample prior to the long-term test.

Due to the extended time period between the most recent field results (November 2000) and when the catalysts were actually removed from the process (January 2001), comparing the field oxidation results to the laboratory results may not be meaningful. The laboratory results show that two of the three catalysts for which oxidation performance was measured were still capable of oxidizing greater than 70% of the inlet elemental mercury, with Carbon #6 oxidizing 91% and the Pd #1 oxidizing 72%. The Fe #1 material reflected a continued loss of activity with time at Site 3, as had been seen in the October and November results. However, the laboratory

Table 4-14
Comparison of Laboratory Test Results for Recovered Catalysts to Site 3 Long-term Results

Catalyst	Laboratory Results for Recovered Catalysts			November Field Results, Elemental Hg Oxidation (%)
	Mercuric Chloride Adsorption Capacity (mg/g sorbent)	Elemental Hg Adsorption Capacity (mg/g sorbent)	Elemental Hg Oxidation (%)	
Fe #1	>220	9	18	45
Carbon #6	490	100	91	85
Pd #1	54	3	72[1,2]	87[3]
Subbituminous Ash #5	150	>170	-	-
Sand Bed Blank	<1	<1	1	36

[1] Loss of flow across the catalyst bed in field apparatus may have adversely affected performance.
[2] Both catalyst beds combined prior to analysis.
[3] First of two catalyst beds in series.

performance of these materials is not necessarily an indicator of their end-of-test performance, as catalysts recovered from the previous two sites generally performed better in the laboratory simulation gas than they had when recovered from the field apparatus. It is speculated that trace species may desorb from the recovered catalysts into the simulation gas, which does not contain such species, partially restoring catalyst activity.

Also, for the Pd #1, it must be noted that a plug in the field apparatus resulted in the loss of flue gas flow across the two sand beds in series. It is likely that in this zero-flow situation, but in the presence of an oxidation catalyst and an ample supply of oxidizing species in the trapped flue gas (e.g., oxygen), the Pd #1 activity was adversely affected by species such as sulfuric acid forming and condensing onto the catalyst surface.

The mercury oxidation data for the sand bed recovered from the Site 3 long-term test are somewhat puzzling. In the field, the oxidation measured across this sand bed "blank" continued to increase with time, with the November percentage measuring at 36% and higher percentages being measured later in the test. However, in the lab, the measured oxidation of elemental mercury across the sand was insignificant, at 1%.

There are at least two possible explanations for this performance. One is that some trace species in the actual flue gas (e.g., selenium) was interacting with the sand to produce a catalytic effect. The laboratory simulation gas was relatively pure and did not contain such trace species. The other, more likely explanation is a fly ash effect. The FGD inlet flue gas at Site 3 contained considerably more fly ash than did the flue gases at Sites 1 and 2. The fly ash at Site 3 was measured to have a relatively high LOI content (typically greater than 5%) and was observed to be reactive for adsorbing and oxidizing mercury. Although the long-term test apparatus had a

filter upstream of the catalyst beds to remove fly ash, the filter membrane used had a 0.45-micron pore size. It is possible that sub-micron fly ash particles, rich in carbon, penetrated the filter with time. Such particles would collect on the walls of the quartz tubing between the filter and the upstream sand beds, and would collect on the quartz wool plug at the inlet to each bed. It is speculated that the observed high mercury oxidation percentages seen across the sand bed as the long-term test progressed was due to fly ash particle buildup with time, and that the oxidation was actually occurring upstream of the sand bed itself. The low elemental mercury concentrations measured in the flue gas at the sand bed inlet (filter outlet) would tend to exacerbate such an effect.

Catalyst regeneration testing was subsequentialy conducted on two catalyst materials recovered from long-term testing at Site 3. Based on the post-field-testing laboratory results, as reported in Table 4-14, the Pd #1 and Fe #1 catalysts were selected for regeneration. Carbon #6 remained highly active and did not appear to warrant regeneration. Subbituminous Ash #5 also appeared to be very active. Since the sample continued to adsorb mercury during the tests summarized in Table 4-14, its elemental mercury oxidation activity could not be measured.

The Pd #1 and Fe #1 catalyst materials were regenerated by heating samples to 700°F (371°C) and purging them with nitrogen for two hours. The regenerated catalysts were then tested in the laboratory for elemental mercury adsorption and oxidation. Results for the regenerated materials are summarized in Table 4-15. The results in Table 4-15 show that the Pd #1 material was effectively regenerated under these conditions, but Fe #1 was not. The regenerated samples did not show significant adsorption capacity for elemental mercury.

Table 4-15
Catalyst Activity Results for Regenerated Catalyst Samples from Site 3

Catalyst Material	Elemental Hg Adsorption Capacity for Regenerated Material (μg/g)	Elemental Hg Oxidation for Regenerated Material, in Simulation Gas (%)	Elemental Hg Oxidation as Recovered from Site 3, in Simulation Gas (%)	Elemental Hg Oxidation for Fresh Material, in Simulation Gas (%)
Fe #1	0	15	18	88
Pd #1	1	89	72	92

Laboratory Tests to Elucidate Catalyst Deactivation Mechanisms

Evaluation of Species Adsorbed on the Catalyst Materials Recovered from Long-term Tests at Site 1

Laboratory tests were performed in an attempt to elucidate the mechanisms involved in catalyst deactivation in the Site 1 flue gas. One hypothesized mechanism was the adsorption or formation of sulfuric acid at the catalyst surface, which may be a poisoning effect that leads to inhibiting mercury oxidation activity. Previous testing by project team members has shown that some

mercury sorbent and catalyst materials are capable of adsorbing SO_2 from simulated flue gases. This often leads to substantial decreases in the surface pH of those sorbents, most likely due to the formation of sulfuric acid through oxidation reactions at the catalyst surface. It is also possible that SO_3 in the flue gas adsorbs directly onto the catalyst surfaces.

Acid leaching tests were performed to determine the amount of acid species removed from flue gas-treated catalysts when they were allowed to equilibrate in water. This test was performed with samples from both the first and second long-term catalyst test at Site 1 and with fresh reagent mixtures. In these tests, a known mass of catalyst/sand sample was added to a fixed volume of water and the slurry was stirred for over 30 minutes. The pH of the equilibrated solutions was measured and used to calculate an acid concentration at the catalyst surface. It was assumed that the acid leached was H_2SO_4 present on catalyst surfaces, and that this H_2SO_4 content represented SO_2 adsorbed from the flue gas.

Table 4-16 summarizes the pH measurements and the calculations of SO_2 adsorbed by each catalyst material. Since the catalyst materials were mixed with sand, the amount of SO_2 adsorbed on the Site 1 sand blank was subtracted from the total amount of SO_2 adsorbed on each catalyst/sand mixture to "back calculate" the amount of SO_2 adsorbed on the catalyst material itself. Table 4-16 indicates the loading for each catalyst per gram of sand.

Figure 4-2 compares the SO_2 adsorption by the different catalyst materials (after correcting for any sand blank contribution). The results indicated that with the exception of Carbon #6, the carbon samples adsorbed the highest levels of SO_2 during both long-term tests. Carbon #6 showed no SO_2 adsorption after correcting for the sand adsorption. This suggests that the surface of this carbon differs from the other carbons such that SO_2 adsorption is inhibited. This did not translate into better mercury oxidation activity, however.

The palladium/alumina sample showed no apparent SO_2 adsorption, as the catalyst/sand mixture showed less SO_2 adsorption than the Site 1 sand blank. Subbituminous Ash #5 showed lower SO_2 pickup than most of the carbons. These results may be significant since the second Site 1 long-term results indicated good long-term reactivity for both of these samples.

It is interesting that for Carbon #1 more SO_2 adsorption occurred in the second bed than in the first. Field results indicated that the first bed was more quickly deactivated (for mercury oxidation) than the second. These results suggest that a gas species other than SO_2 may dominate the catalyst deactivation. It is possible that such a species is adsorbed in the first fixed bed, subsequently making surface sites unavailable for adsorption of SO_2 which then passes on to the second bed.

Additional characterization of the recovered Site 1 samples was performed to determine what species desorb, and in what quantities, in a further attempt to elucidate deactivation mechanisms. The trace species concentrations of fresh catalyst materials, recovered field samples, and regenerated field samples were analyzed. Species adsorbed during field testing were determined by the difference between virgin and recovered field sample concentrations of the species analyzed, and species desorbed during regeneration were determined by the difference between recovered field sample and regenerated sample concentrations.

Table 4-16
Determination of SO$_2$ Adsorbed on Site 1 Long-term Catalysts

Sorbent	Catalyst Loading in Sand (mg/g)	pH		mmoles SO$_2$ Adsorbed on Catalyst/Sand Mixture	mg SO$_2$ Adsorbed on Catalyst	SO$_2$ Adsorbed/g Catalyst (mg/g)
		Fresh Catalyst	Recovered Catalyst			
Materials Recovered from the First Long-term Test at Site 1						
Sand	1000	5.23	3.68	3.0	-	-
Carbon #1 – First Bed	3.33	6.58	3.35	6.7	234	70.2
Carbon #1– Second Bed	3.33	-	3.12	11.4	533	160.1
Carbon #6	3.33	6.36	3.72	2.9	-12	-3.7
Subbituminous Ash #5	20	6.74	2.98	15.7	810	40.5
Carbon #4	3.33	5.85	3.33	7.0	253	75.9
Materials Recovered from the Second Long-term Test at Site 1						
Sand	1000	5.23	3.67	3.1	-	-
Carbon #1 – First Bed	33.3	8.31	2.56	41.3	2444	73.4
Carbon #1 – Second Bed	33.3	-	2.45	53.2	3207	96.3
Pd #1	200	4.34	4.05	0.7	-158	-0.8
Carbon #2	33.3	5.75	2.43	55.7	3365	101.1
Subbituminous Ash #5	200	8.44	2.27	80.6	4956	24.8
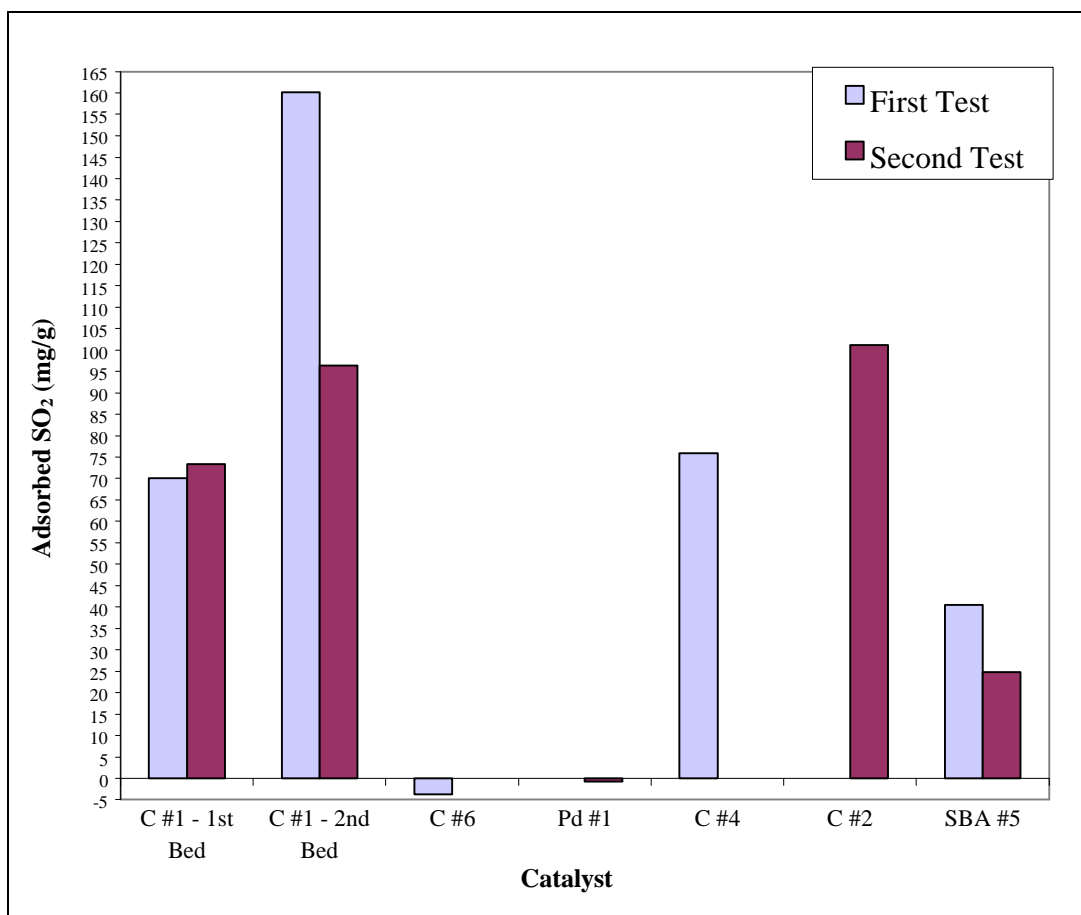
Figure 4-2
Results of Acid Leaching Tests on Catalyst Samples from the First and Second Long-term Tests at Site 1

Examination of the catalyst bulk chemistry results appears to confirm hypotheses that selenium and sulfur (as SO_2 and/or SO_3) are the primary species that adsorbed from the Site 1 flue gas. A summary of the concentration changes for both of these species during the long-term testing at Site 1 is presented in Figure 4-3, and the percent of adsorbed sulfur and selenium which desorbed during subsequent regeneration is shown in Figure 4-4.

In Figure 4-3, comparison of the upstream and downstream field samples of Carbon #1 shows that 50% more sulfur species adsorbed in the second bed while 150% more selenium adsorbed in the first bed. The sulfur results qualitatively confirm the relative acid leaching results presented in Table 4-16 for these two samples. However, Subbituminous Ash #5 showed higher sulfur adsorption quantities than either Carbon #1 samples in Figure 4-3, but indicated significantly lower sulfur adsorption in the acid leaching test results presented in Table 4-16. This may be because adsorbed sulfur species reacted with metals in the fly ash to form neutral salts, which would not contribute to lowered pH in the acid leaching test.
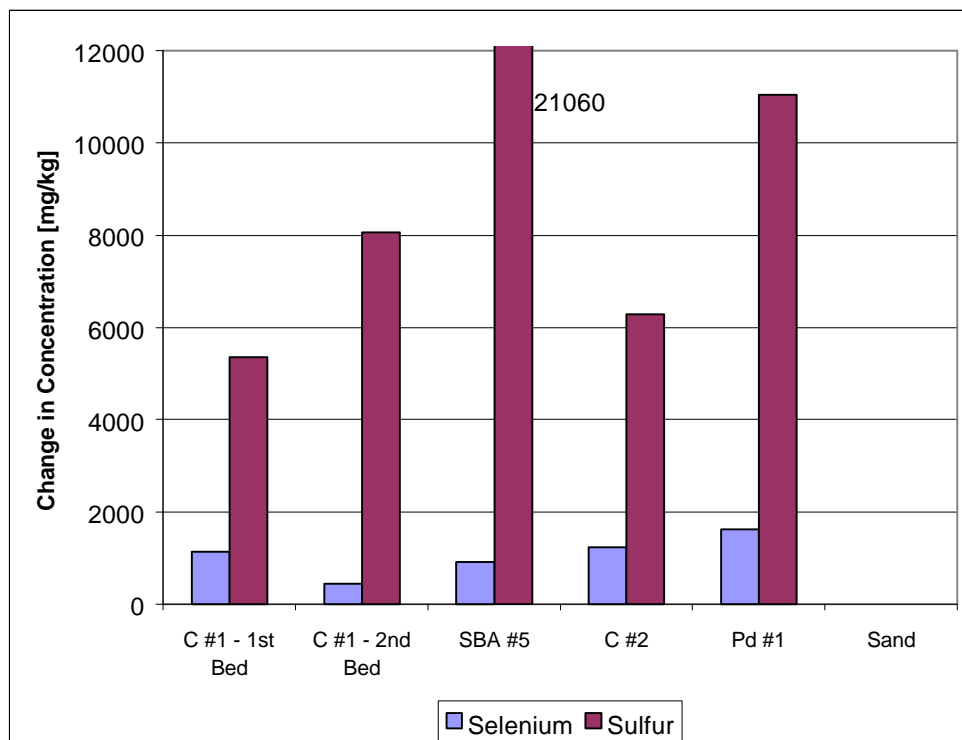
Figure 4-3
Measured Increases in Selenium and Sulfur Concentrations During Field Testing at Site 1 (Samples from Second Long-term Test)
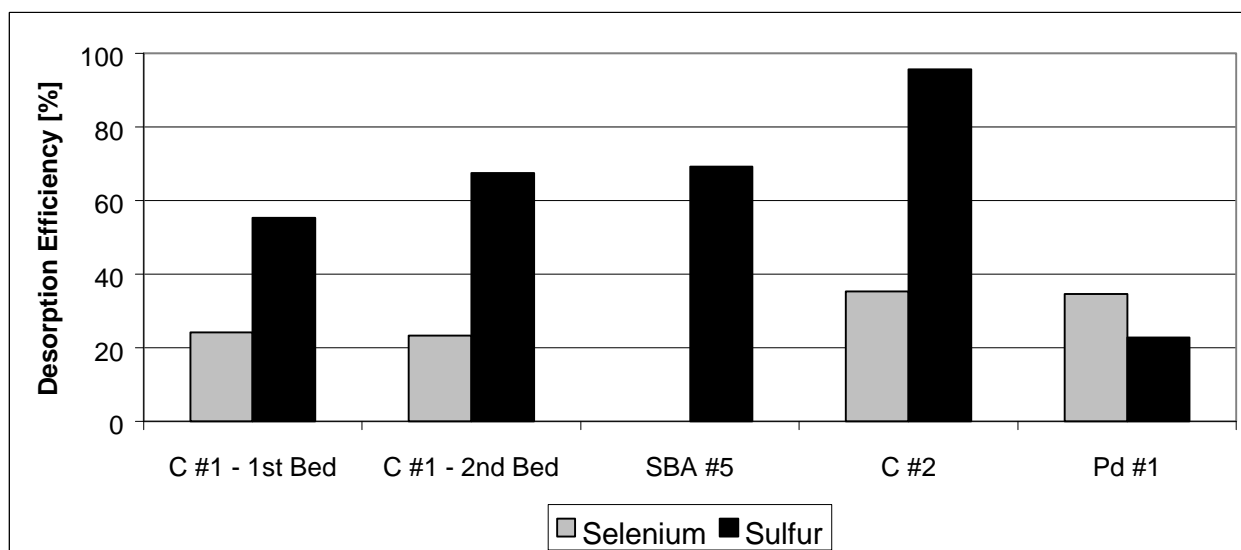
Figure 4-4
Percent of Adsorbed Material that Desorbed during Regeneration with CO_2 at 700°F (371°C) (Samples from Second Long-term Test)

Figure 4-4 shows the percentages of sulfur and selenium desorbed from each catalyst based on chemical analyses of field samples and laboratory regenerated material. The desorption efficiency is the amount of material adsorbed during field testing which subsequently desorbed during regeneration. If a substance poisons a catalyst, then 100% desorption efficiency of this substance could signify complete regeneration of that catalyst. However, some adsorbed species may enhance catalyst performance; in this case, 100% desorption efficiency might be undesirable.

The two Carbon #1 samples exhibited similar desorption efficiencies for selenium, at only about 25% of the amount originally adsorbed on each. The downstream Carbon #1 sample exhibited a higher SO_2 desorption efficiency than did the upstream Carbon #1, at about 70% desorbed versus 55%. The results in Figure 4-3 showed that the downstream Carbon #1 sample had adsorbed about 50% more sulfur than had the upstream bed, so considerably more sulfur desorbed from the downstream sample than from the upstream sample. Figure 4-3 shows that Carbon #2 adsorbed sulfur species in a quantity between those of the two Carbon #1 beds, but desorbed SO_2 more efficiently than either of the Carbon #1 samples (almost 100% desorption for Carbon #2).

The results in Figures 4-3 and 4-4 show that Pd #1 tends to capture SO_2 and not readily desorb it upon regeneration. The carbon samples all showed more efficient desorption of sulfur than of selenium while the Pd #1 catalyst showed the opposite result.

The Subbituminous Ash #5 sample analyses showed higher selenium concentrations in the regenerated sample than in the field sample from Site 1, hence no desorption shown in Figure 4-4. Since this does not seem to be physically possible, it raises some concern over the accuracy of the results. This unexpected result was seen for several trace species. The solid samples tested in these experiments were analyzed using two different digestion methods to improve the accuracy for different trace metals present. However, the tests still show higher concentrations of some species in the regenerated samples than in the field samples, which does not seem physically possible. It is likely that these results indicate a measurement bias. Analysis of aluminum concentrations in the catalysts proved to be particularly difficult, especially for the Pd #1 catalyst.

Recovered field samples from the long-term tests at Site 1 were tested for post-field performance in simulation gas, acid leaching as an indicator of SO_2 adsorption, and bulk concentration changes. These results have shown that sulfur oxides and selenium adsorbed on the catalysts recovered from Site 1 and desorb upon regeneration. Results were inconclusive about other trace species. Only selenium has been identified as a trace species adsorbed on spent catalysts that desorbs upon regeneration. Although the sulfur oxides behave in the same manner, SO_2 is present in the simulation gas and should not affect catalyst activity in the laboratory compared to field results. Thus, selenium remains the leading candidate for being an adsorbed species in the spent catalysts that is not present in the simulation gas. Desorption of selenium in the laboratory runs could explain the high adsorption capacity and oxidation activity of the previously spent catalyst materials, but this mechanism has not been confirmed.

Leaching of Acid from Samples Recovered from Site 2

Samples recovered from the three-week screening test at Site 2 were tested to determine the amount of SO_2 adsorbed while treating flue gas. Acid leaching tests were carried out by the procedure described above for the Site 1 samples. The amount desorbed was assumed to represent all of the adsorbed acid species on each catalyst, and the desorbing acid was assumed to all be due to SO_2 adsorption on the catalyst surface (there is virtually no SO_3 present in the Site 2 flue gas). These tests were repeated two to four times to improve accuracy. Figure 4-5 shows the average amount of SO_2 adsorbed for each catalyst.
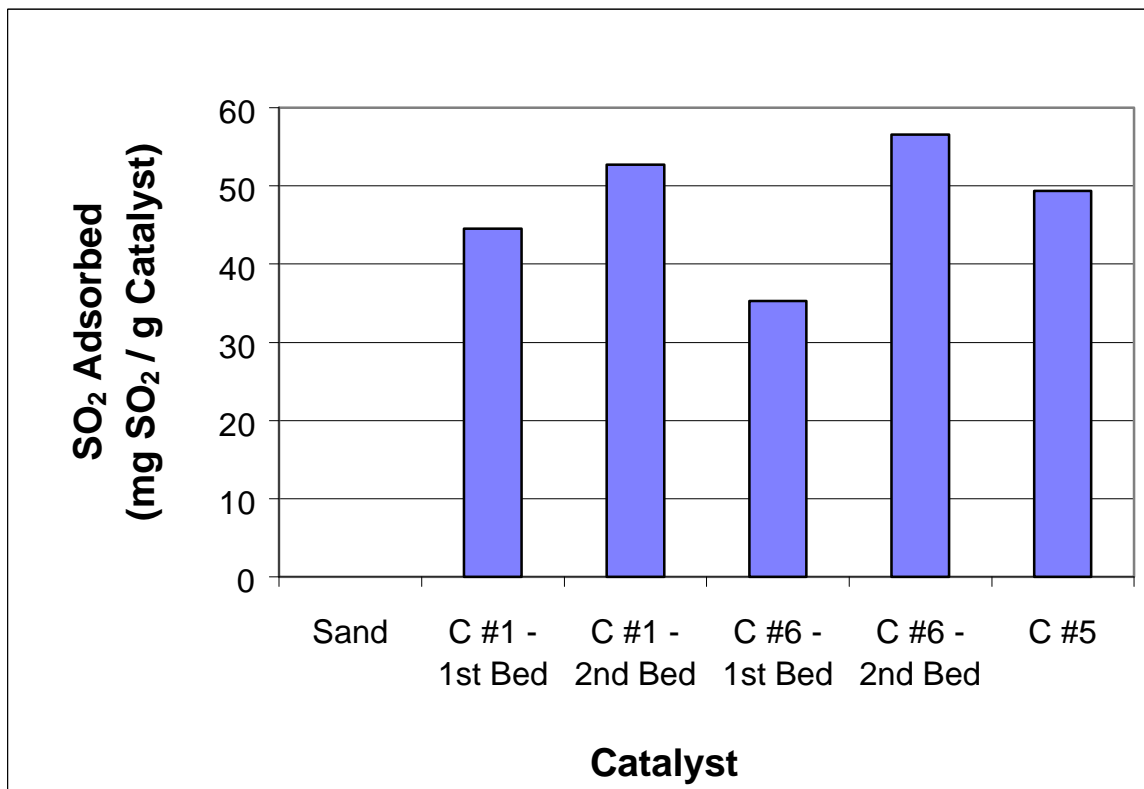
Figure 4-5
Results of Acid Leaching Tests for Set 5 Short-term Catalysts at Site 2

The sand blank showed negligible SO_2 adsorption, and all catalyst samples showed SO_2 adsorption levels within the same order of magnitude. The Carbon #1 SO_2 concentrations are approximately one third to one half of the concentrations determined by conducting the same analysis on the Site 1 long-term samples. Lower SO_2 concentration in the Site 2 gas probably caused this difference; the typical uncontrolled SO_2 concentrations in Site 1 and Site 2 flue gas are 1450 ppm and 300 ppm, respectively. Carbon #5 was not tested at Site 1, so no similar comparison can be made.

In the Site 1 leaching tests, Carbon #1 desorbed much more SO_2 than Carbon #6, which is not the case for the Site 2 results. Carbon #6 showed no apparent acidity after exposure to Site 1 flue gas, but significant acidity after the Site 2 exposure. This is surprising since both the exposure

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time and flue gas SO2 concentrations were higher at Site 1. The competing adsorption of selenium from the Site 1 flue gas may have influenced this comparison, though.

It is interesting that for both carbons in which two beds were tested in series, the second bed apparently adsorbed more SO_2 (i.e., acidic species) than the first bed. Similar results were obtained for Carbon #1 from the long-term testing at Site 1. Although it is not known what causes this phenomenon, it suggests that SO_2 adsorption in the first bed may be limited by the competing adsorption of other flue gas species at the catalyst surfaces.

Evaluation of Species Adsorbed on the Catalyst Materials Recovered from Long-term Tests at Site 3

Two different types of laboratory tests were conducted to investigate potential mechanisms for catalyst loss of activity at Site 3. One series of tests investigated the leaching of acid species from the catalyst surfaces into deionized water. The resulting leachate was analyzed for pH drop, indicative of overall acid species concentrations, and for anions associated with common flue gas acid gas species (sulfate [sulfuric acid] and chloride [hydrochloric acid]).

In the second laboratory investigation, during the catalyst regeneration tests, the effluent gases were sampled and analyzed to determine if selenium or other chemicals were adsorbed on the catalysts prior to regeneration and may have contributed to their deactivation. Recall that selenium appeared to have correlated with decreased oxidation activities of catalyst materials at Site 1, and the Site 3 flue gas was measured to have even higher gas-phase selenium concentrations than at Site 1.

To conduct these analyses, the effluents from the catalyst regeneration tests were passed through a solution of nitric acid and peroxide to capture emitted species. These solutions, as well as a portion of the catalyst solids from before and after regeneration, were sent to a third-party laboratory for analyses of trace metals content.

<u>Leaching of Water-soluble Acids from Catalyst Materials</u>. Catalyst samples recovered from the long-term test at Site 3 were tested for water-soluble acid content according to a leaching procedure used on samples from all three sites. One gram of catalyst/sand mixture (or of the sand bed blank) was stirred in 30 ml of deionized water, and the equilibrium pH was measured. From the resulting pH value, a water-soluble acid content was calculated, and this acid content was expressed as a quantity of adsorbed SO_2 (assuming SO_2 or SO_3 would be the primary adsorbing acid species at these sites). The results of these acid leaching tests are summarized in Table 4-17. Where the same catalyst type had been tested at the other sites and acid leaching tests were conducted, the results from those sites are also summarized in the table. For the Site 3 samples, additional analyses were conducted that had not been conducted for the samples from Sites 1 and 2: the leachate was analyzed by ion chromatography (IC) for sulfate and chloride ion content. These results are also shown in Table 4-17.

The results show that for all three sites, the pH drop for the sand blank samples indicate a negligible amount of adsorbed, water-soluble acid on the sand itself. The pH drop data also show very little water-soluble acid on the Pd #1 catalyst, but significant quantities on the

Table 4-17
Acid Leaching from Recovered Catalyst Samples into Deionized Water

Catalyst Type	Site 1 Data Adsorbed SO$_2$ (mg/g) Estimated from pH Drop	Site 2 Data Adsorbed SO$_2$ (mg/g) Estimated from pH Drop	Site 3 Data			
			pH	Adsorbed SO$_2$ (mg/g) Estimated from pH Drop	Adsorbed SO$_2$ (mg/g) from IC Data	Adsorbed Cl (mg/g) from IC Data
Sand Blank	0.003	0.045	4.38	0.040	2.9	-
Fe #1	-	-	2.68	39.7	368	1.8
Pd #1	0	-	4.00	1.5	407	3.3
Subbituminous Ash #5	25-41	-	2.74	85.3	346	1.6
Carbon #6	0	35-57	3.60	60.7	305	19.1

Subbituminous Ash #5 samples (Sites 1 and 3 samples). For the latter, the amount of water-soluble acid on the sample from Site 3 is greater than that from Site 1, which was expected based on the higher coal sulfur content at Site 3. These results are consistent with previous URS tests that have shown higher levels of absorbed leachable acidic species in carbon-derived samples than in samples not containing carbon.

The Carbon #6 catalyst is the only one for which water-soluble acid leaching data are available from all three sites, and these data show inconsistencies. The Site 3 sample showed the highest content of water-soluble acid, as would be expected. The Site 2 sample showed the next highest quantity, ranging from about 60% of the Site 3 value in the upstream bed to over 90% of the Site 3 value in the downstream bed of two in series. The Site 1 sample, which was exposed to flue gas with SO$_2$, SO$_3$ and HCl contents between those of Sites 2 and 3, showed essentially no water-soluble acid. Thus, these data do not follow the expected order based on the sulfur and/or chloride contents of the coals fired at these sites. However, results at Site 1 indicated that high levels of absorbed selenium may have blocked the carbon surface from sulfur absorption, thus explaining these results.

The sulfate and chloride data for the water leachates of the Site 3 samples are surprising, in that the amount of water-soluble sulfates leaching from these samples far exceeds the amount of acid leaching based on the observed pH drop data. Thus, most of the sulfates must be present as water-soluble salts rather than as sulfuric (or sulfurous) acid. In the case of the Pd #1 sample, even the chloride content exceeds the amount of acid potentially present as HCl based on the pH drop data (not shown in the table), indicating the chlorides must be present as salts, too.

It is clear from these data that the catalyst materials adsorb water-soluble acids, sulfates and/or chlorides from the flue gas treated in varying amounts. It is less clear, though, whether this adsorption has any relationship with catalyst activity or loss of activity with time. For example, the Fe #1 catalyst, which saw the greatest loss of activity in the long-term test at Site 3, tended to

fall in the middle of the range of samples with respect to the amount of adsorbed water-soluble acid species, sulfates, and chlorides. If there were a relationship with loss of activity, we would have expected the Fe #1 results to fall at one extreme (high or low) for one of these parameters.

Trace Metals Analyses of Recovered and Regenerated Catalysts. The catalyst materials recovered from the long-term test at Site 3 were also analyzed for trace metal concentrations. These analyses were conducted to determine if relationships could be established between adsorbed trace metal content and deactivation. The results of these analyses are summarized in Table 4-18. The concentrations shown are as measured for the sand bed/catalyst mix. Assuming the metals are actually adsorbed on the catalyst materials and not on the sand, the concentrations in the catalysts themselves would be much higher than the values shown in Table 4-18.

The metals most prevalent on the recovered catalysts are selenium, and metals commonly associated with fly ash (aluminum, calcium, iron, magnesium, potassium, and sodium). These are also the metals that were most prevalent in the Site 3 flue gas as measured by Method 29, so it might be expected that they would be adsorbed on the catalyst materials. Only thallium was found in significant concentrations in the Site 3 flue gas (8 ppb) but not adsorbed on any of the catalysts to a significant concentration. Fe #1 also had significant concentrations of other metals, which were most likely incorporated into the base catalyst metal. Besides iron and chromium, these included copper, lead, manganese, nickel, and zinc.

As mentioned above, regeneration tests were carried out on both the Pd #1 and Fe #1 catalysts. As part of this testing, the regeneration gas exiting the bed was passed through impinger solutions to recover metal species evolving from the catalyst surfaces. Trace metals analyses were conducted on these impinger solutions, as well as on samples of the catalyst solids from after the regeneration process. These analyses were conducted to determine if relationships could be established between desorption of metals and restored activation.

Similar analyses were conducted on the recovered and regenerated catalysts from Site 1. Those analyses indicated that selenium and sulfur were the two main species adsorbed by the catalyst/sand mixtures, and that those species desorbed during regeneration. While it could not be concluded what species most contributed to catalyst deactivation at Site 1, it was speculated to be selenium or sulfur, or both.

For the catalysts from the long-term test at Site 3, the amounts of sulfur adsorbed by the catalysts were quantified by the acid leaching procedure described in the previous subsection. The amounts of selenium and other metals that desorbed on regeneration were quantified by the trace metals analyses described above. The results from those analyses are presented in Table 4-19.

Trace quantities are shown for the original catalyst/sand mixtures recovered from the long-term test at Site 3, for the regenerated material, and for the impinger catches from the regeneration gas. Metals material balance closures are shown in terms of the total amount recovered after regeneration (regenerated solids plus impinger catch) compared to the amount measured in the catalyst prior to being regenerated. The percent closures are within ±20% for about 2/3 of the metals for which the solid phase analyses were above detection limits, which is relatively good closure for trace metals analyses. The other thing to note in the table is that, like the metals found

Table 4-18
Trace Metal Concentrations in Catalyst/Sand Beds Recovered from Site 3 Long-term Test

Trace Metal	Fe #1, mg/kg of Sand Bed	Pd #1, mg/kg of Sand Bed	Subbituminous Ash #5, mg/kg of Sand Bed	Carbon #6, mg/kg of Sand Bed
Al	131	11,500	389	233
Sb	2.98	<0.272	<0.249	0.125
As	<0.122	0.410	0.240	0.622
Ba	0.559	0.318	19.5	0.593
Be	0.0174	0.00957	0.0195	0.0137
Cd	0.241	<0.019	<0.017	<0.019
Ca	288	31.0	500	39.6
Cr	1790	0.863	0.922	1.62
Co	1.00	0.267	<0.039	1.27
Cu	17.0	2.14	0.850	0.921
Fe	21,200	71.2	174	100
Pb	12.1	0.411	0.643	0.529
Mg	77.2	19.3	106	27
Mn	130	0.240	0.515	0.992
Mo	<0.075	0.627	<0.073	0.119
Ni	16.8	0.632	0.274	1.94
K	9.66	12.0	15.7	20.6
Se	144	59.0	62.9	1.34
Ag	<0.092	<0.099	<0.091	<0.101
Na	177	<42.3	110	181
Sr	2.35	1.44	10.7	1.64
Tl	<0.158	<0.170	<0.155	<0.173
Ti	2.62	17.8	22.0	12.6
V	0.273	0.207	0.632	0.209
Z	384	14.1	0.599	64.9

Table 4-19
Trace Metals Analyses of Site 3 Catalysts – Pre- and Post-Regeneration

Trace Metal	Fe #1				Pd #1			
	After Long-term, mg/kg	Regen-erated, mg/kg	Impinger mg/kg	Mass Balance Closure (Regen/ Prior)	After Long-term, mg/kg	Regen-erated, mg/kg	Impinger mg/kg	Mass Balance Closure (Regen/ Prior)
Al	131	205	0.53	157%	11500	8210	1.66	71%
Sb	2.98	2.75	<.01	93%	<0.272	<0.275	<0.011	-
As	<0.122	<0.112	<.01	-	0.410	0.498	<0.007	123%
Ba	0.559	0.74	0.004	133%	0.318	0.264	0.01	88%
Be	0.0174	0.0112	<0.0002	65%	0.00957	<0.004	<0.0002	<48%
Cd	0.241	0.287	0.01	122%	<0.019	<0.019	0.004	-
Ca	288	291	1.76	102%	31.0	18.8	1.92	67%
Cr	1790	1630	0.01	91%	0.863	0.846	0.02	100%
Co	1.00	0.939	<0.002	94%	0.267	0.237	<0.002	90%
Cu	17.0	15.7	<0.001	92%	2.14	1.07	0.01	51%
Fe	21200	19100	0.09	90%	71.2	58.1	0.61	82%
Pb	12.1	10.7	0.04	89%	0.411	0.364	0.01	90%
Mg	77.2	84.5	0.11	110%	19.3	10.8	0.32	58%
Mn	130	117	0.01	90%	0.240	0.265	0.01	115%
Mo	<0.075	<0.068	0.01	-	0.627	0.432	<0.004	69%
Ni	16.8	15.9	0.02	95%	0.632	0.569	0.08	103%
K	9.66	12.5	<.05	130%	12.0	9.4	0.67	84%
Se	144	113	22.9	94%	59.0	40.5	1.41	71%
Ag	<0.092	<0.085	<0.002	-	<0.099	<0.1	0.003	-
Na	177	247	3.16	141%	<42.3	<42.9	6.73	-
Sr	2.35	2.7	0.005	115%	1.44	1.15	0.01	80%

Table 4-19
Trace Metals Analyses of Site 3 Catalysts – Pre and Post Regeneration (continued)

Trace Metal	Fe #1				Pd #1			
	After Long-term, mg/kg	Regen-erated, mg/kg	Impinger mg/kg	Mass Balance Closure (Regen/ Prior)	After Long-term, mg/kg	Regen-erated, mg/kg	Impinger mg/kg	Mass Balance Closure (Regen/ Prior)
Tl	<0.158	<0.145	<0.011	-	<0.17	0.215	<0.012	>133%
Ti	2.62	3.94	0.01	151%	17.8	14.3	0.07	81%
V	0.273	0.319	<0.002	117%	0.207	0.0868	<0.002	43%
Z	384	362	0.14	94%	14.1	9.79	0.17	71%

in the highest concentrations on the recovered catalysts, those found desorbed in the impinger solutions are selenium, alumina, calcium, iron, magnesium, potassium, and sodium.

The previous Site 1 results showed that selenium was the most prevalent adsorbed metal species on deactivated catalysts, and that selenium readily desorbed during regeneration. It was speculated that selenium might play a role in catalyst deactivation mechanisms. However, a comparison of catalyst activity at the end of the long-term tests versus the amount of selenium adsorbed on each catalyst does not readily support this hypothesis. This comparison is made for the long-term test catalysts from Sites 1 and 3 in Table 4-20. The catalyst activity data are somewhat confounded, though, because of measurement issues at the end of the long-term tests at both of these sites that interfered with the ability to accurately measure catalyst activity in the field. The activity measured for the recovered materials in the lab, on simulated flue gas, is also shown in the table.

However, since the simulation gas does not contain selenium and selenium may have desorbed from the catalyst during these activity tests, the lab activity results may not be meaningful for this comparison.

Several inconsistencies are noted in the results summarized in Table 4-20. First, the adsorbed selenium concentrations are higher in the catalysts recovered from Site 1, in spite of the fact that Method 29 measurements showed higher selenium concentrations in the flue gas at Site 3. The catalyst concentration data are supported by anecdotal observations that the desorption gas turned downstream tubing and glassware pink during the Site 1 catalyst regeneration tests (an indicator of high selenium concentrations), whereas this phenomenon was not observed for the Site 3 regenerations. These observations call into question the Method 29 results for gas phase selenium concentration at Site 3 as possibly being biased high. Another possible explanation is that the higher SO_2 levels at Site 3 inhibited the absorption of selenium to the catalyst surface as compared to Site 1.

Table 4-20
Comparison of Selenium Concentrations for Catalyst Materials from Long-term Tests at Sites 1 and 3

Catalyst Type	Long-term Test Site	Selenium in Flue Gas, ppb	Selenium Adsorbed on Catalyst, mg/g catalyst	Catalyst Activity at End of Test, % Oxidation of Elemental Hg	
				Field Result	Lab Result
Pd #1	1	27	8.1	0	80
Subbituminous Ash #5	1	27	4.9	0	24
Carbon #1	1	27	33.8	89*	47
Carbon #2	1	27	36.8	76*	74
Pd #1	3	45	1.5	87**	72
Carbon #6	3	45	0.4	85**	91
Fe #1	3	45	2.9	45**	18
Subbituminous Ash #5	3	45	3.1	-	-

* Value suspect because of apparent measurement bias.
** November 2000 result; test concluded at the end of January 2001.

When the activity data are compared with selenium concentrations, data quality issues make it difficult to determine the impact of adsorbed selenium. For Pd #1, the Site 1 catalyst had over five times the selenium concentration of the Site 3 catalyst. In the field, the Site 1 catalyst had lost all activity (possibly due to a low-temperature excursion), while the Site 3 catalyst remained active (although last measured two months before the catalyst was recovered). To the extent that these are valid comparisons of field performance, the relative activity of these two samples is consistent with adsorbed selenium contributing to loss of activity. In the laboratory results with the recovered field samples, though, the Site 1 catalyst was actually more active than the Site 3 catalyst.

Similarly, the Subbituminous Ash #5 sample from Site 1 had more selenium content than the sample from Site 3. The Site 1 sample showed no activity in the field and low activity in the laboratory at the end of the test. The Site 3 sample could not be measured for activity in the field or in the laboratory; in the field because of high activity by the upstream catalyst bed, and in the laboratory because the sample was adsorbing significant quantities of mercury throughout the activity test. Assuming the Site 3 sample continued to be active, given that it was still adsorbing mercury, the Site 1 versus Site 3 results again support the hypothesis that adsorbed selenium adversely affects activity.

For the other catalyst materials, no two were tested at both sites, so it is not possible to make direct comparisons. It is possible to make some observations from these data. For example, the most active of the Site 3 recovered catalysts, Carbon #6, had the lowest adsorbed selenium content, while the least active, Fe #1, had almost the highest. In another comparison, the carbons from Site 1 had adsorbed almost two orders of magnitude more adsorbed selenium than Carbon #6 from Site 3, yet they retained some activity towards mercury oxidation. However, since the catalytic oxidation mechanisms may differ among the catalyst types, it may not be meaningful to compare absolute concentrations of adsorbed selenium from one catalyst type to the another.

Table 4-21 compares the selenium desorption results for the two catalysts from Site 3 that were regenerated. Based on the solids analyses from before and after regeneration, the Fe #1 catalyst desorbed about 22% of the adsorbed selenium, while Pd #1 desorbed approximately 31%. The Pd #1 activity was restored by the regeneration process, while the Fe #1 activity was not, so these data at least directionally support the premise that adsorbed selenium contributes to a loss of activity, while desorbing selenium on regeneration restores activity.

Table 4-21
Comparison of Selenium Desorption Versus Activity Towards Elemental Mercury Oxidation in Regenerated Site 3 Catalysts

Catalyst	Selenium in Recovered Catalyst, mg/g catalyst	Selenium in Regenerated Catalyst, mg/g catalyst	Reduction in Selenium Concentration %	Elemental Mercury Oxidation by Recovered Catalyst, % (lab result)	Elemental Mercury Oxidation by Regenerated Catalyst, % (lab result)
Fe #1	2.9	2.3	22	18	15
Pd #1	1.5	1.1	31	72	89

Other Laboratory Tests

Effects of Simulation Gas Composition

The laboratory catalyst screening results for Site 2, as presented previously in Table 4-5, all were generated using a simulation gas with 1 ppm of HCl. Earlier bench-scale tests performed with no HCl in the simulation gas generally showed poor catalyst performance, suggesting the participation of HCl in the mercury adsorption and oxidation mechanisms. A comparison of lab results with and without HCl in the simulation gas is shown in Table 4-22. While the performance of most catalyst materials improved when 1 ppm of HCl was added to the simulation gas, some showed no change, and the performance of some degraded. One of the iron-based catalysts, Fe #1, showed the greatest loss of activity, suggesting that HCl is a poison for that particular catalyst.

Laboratory experiments were also conducted to examine the effect of NO_X concentration (primarily NO) on the mercury adsorption and oxidation performance of three catalyst materials. Phase I results showed that it was important that NO_X be present in the laboratory simulation gas

Table 4-22
Equilibrium Adsorption Capacity and Mercury Oxidation for Catalysts in Site 2 Simulation Gas with and without 1 ppm HCl

Sample Type	Sample	Sample Loading (mg Sample/ g Sand)	Adsorption Capacity (μg Hg^0/g Sample)		Mercury Oxidation (% Inlet)	
			No HCl	1 ppm HCl	No HCl	1 ppm HCl
Carbon	Carbon #1	2	28	624	1	77
	Carbon #2	2	1549	1308	89	80
	Carbon #3	2	157	266	49	63
	Carbon #4	2	58	29	0	11
	Carbon #5	2	5741	5911	32	0
	Carbon #5a	2	86	80	2	79
	Carbon #6	2	258	401	55	100
	Carbon #6a	2.2	97	614	0	100
Fly Ash (Bituminous)	Bituminous Ash #2a	20	0	2	0	34
	Bituminous Ash #3	20	3	0	0	88
	Bituminous Ash #16	20	1	0	11	0
Fly Ash (Subbituminous)	Subbituminous Ash #1	20	0	0	1	0
	Subbituminous Ash #2	20	0	0	0	0
	Subbituminous Ash #3	20	1	3	0	28
	Subbituminous Ash #4	20	2	11	17	96
	Subbituminous Ash #5	2,20	56	150	2	70
Fly Ash (Lignite)	Lignite Ash #1	20	1	0	6	0
	Lignite Ash #3	20	11	0	6	0
Fly Ash (Oil)	Oil-fired Ash	20	0	0	18	0

Table 4-22
Equilibrium Adsorption Capacity and Mercury Oxidation for Catalysts in Site 2 Simulation Gas with and without 1 ppm HCl (continued)

Sample Type	Sample	Sample Loading (mg Sample/ g Sand)	Adsorption Capacity (µg Hg^0/g Sample)		Mercury Oxidation (% Inlet)	
			No HCl	1 ppm HCl	No HCl	1 ppm HCl
	Oil-Fired Ash #2	20	0	0	0	81
Metal/Catalyst	Fe #1	20	8	7	57	8
	Fe #2	20	1	0	0	0
	Fe #3	20	0	0	16	0
	Ni #1	2,20	7	0	4	0
	Pd #1	20	26	30	77	90
	Pd #3	20	7	4	96	95
	SCR	20	3	3	10	0
	Zn #1	20	0	0	0	0

when evaluating mercury catalysts. Since the range of NO_X concentrations encountered at coal-fired units could range from very low concentrations for units with selective catalytic reduction to very high for cyclone-fired units, these tests were conducted to determine how variations in flue gas NO_X concentration affected catalyst performance.

These NO_X effect results are presented in Table 4-23. The baseline gas for these tests was simulated Site 2 gas containing 1 ppm of HCl. The results show that increasing the NO_X concentration to as high as 800 ppm decreased Carbon #1 catalyst oxidation performance slightly and greatly reduced its adsorption capacity. However, when no NO_X was present, the oxidation performance of Carbon #1 was worse than even at the high NO_X concentration. These results suggest that, like HCl, NO_X plays a role in the catalytic oxidation of mercury.

For Subbituminous Ash #5 and Pd #1, the role of NO_X was less dramatic. For Subbituminous Ash #5, the adsorption capacity appeared to generally increase with NO_X concentration. As for Carbon #1, the oxidation percentage appeared to decrease at the highest NO_X concentration and even more so with no NO_X present. However, the effect was less pronounced than for Carbon #1. For Pd #1, the adsorption capacity appeared to decrease with increasing NO_X concentration. As with the other catalysts tested, the oxidation performance measured was lowest with no NO_X in the simulation gas, and there was a slight reduction in performance at the highest NO_X concentration.

Table 4-23
Effect of NO$_X$ Concentration on the Performance of Carbon #1 at 300°F (149°C), Site 2 Simulated Conditions (with HCl)

NO$_X$ Concentration (ppm)	Carbon #1		Subbituminous Ash #5		Pd #1	
	Adsorption Capacity (µg Hg^0/g Sample)	Elemental Hg Oxidation (% Inlet)	Adsorption Capacity (µg Hg^0/g Sample)	Elemental Hg Oxidation (% Inlet)	Adsorption Capacity (µg Hg^0/g Sample)	Elemental Hg Oxidation (% Inlet)
0	1230	58	287	81	41	72
10	-	-	-	-	29	91
25	1192	98	-	-	21	96
50	-	-	309	100	-	-
100	1979	88	323	94	10	91
200	624	88	145	100	30	89
400	776	88	325	96	-	-
600	587	69	322	96	8	89
800	284	77	433	83	5	86

These results agree with the Phase I finding that the laboratory simulation gas must contain NO$_X$ to adequately simulate field performance. They also suggest that, while NO$_X$ appear to plays a role in mercury oxidation, over the range of NO$_X$ concentrations encountered in most pulverized coal boilers, the actual NO$_X$ concentration in the flue gas will not greatly impact mercury catalyst performance.

A number of tests were conducted with Carbon #1 to determine the effects of the form of the NO$_X$ present (predominantly NO for the "NO$_X$" tests vs. all NO$_2$). The results of these tests are summarized in Table 4-24. Table 4-24 also includes the results from Table 4-23 on the effects of NO$_X$ (predominantly NO) on the performance of Carbon #1. The results show that NO$_2$ significantly lowers catalyst adsorption capacity relative to that with NO, but its effects on mercury oxidation are almost identical to those of NO. This suggests that the NO-to-NO$_2$ ratio in the laboratory simulation gas or in actual flue gases encountered in the field will not greatly impact catalyst oxidation results.

Effect of Palladium Loading on Honeycomb Catalyst Structures

As described in Section 3, mass transfer calculations were conducted to model elemental mercury conversion in the honeycomb reactor versus the pellet reactor. For these calculations, the reaction rate was assumed to be instantaneous at the catalyst surface (i.e., reaction kinetics were assumed not to control the overall reaction rate). The calculations were conducted to

Table 4-24
Effect of NO$_2$ Concentration on the Performance of Carbon #1 at 300°F (149°C), Site 2 Simulated Conditions (with HCl)

NO$_X$/NO$_2$ Concentration (ppm)	NO$_X$ Predominantly as NO		NO$_X$ Present as NO$_2$	
	Adsorption Capacity (µg Hg^0/g Sample)	Elemental Hg Oxidation (% Inlet)	Adsorption Capacity (µg Hg^0/g Sample)	Elemental Hg Oxidation (% Inlet)
0	1230	58	1072	47
5	-	-	1275	100
10	-	-	894	98
20	-	-	299	97
25	1192	98	-	-
30	-	-	339	100
40	-	-	213	95
50	-	-	337	90
100	1979	88	99	87

provide an indication of the extent to which mercury diffusion from the flue gas to the honeycomb surface could be controlling the overall conversion, relative to the pellet catalyst form. These results showed that at similar area velocities, the mass transfer correlations predict higher oxidation efficiencies for the pellet catalyst form, suggesting that diffusion of mercury from the bulk gas to the honeycomb surface controls reaction rates for the honeycomb form.

When the oxidation efficiencies measured for the pellet and honeycomb catalysts at Site 2 were expressed in terms of number of mass transfer units, the measured performance of the pellet catalyst was, on average, closer to predicted values than was the measured performance for the honeycomb. This suggests that the assumption of instantaneous reaction rates at the catalyst surface was reasonable for the pellets, but less so for the honeycomb. It was speculated that the palladium loading on the honeycomb surface tested at Site 2 was inadequate to ensure rapid reaction rates. Laboratory tests on honeycomb samples with higher palladium loadings were conducted to determine if this was, in fact, the case.

Initial laboratory tests were conducted with the honeycomb samples used in slipstream tests at Site 2. The normal synthetic gas flow rate in the laboratory apparatus (1 L/min) is only about 10% of the flow rate at which these honeycomb catalyst samples were operated in the field. At the relatively low flue gas rate and correspondingly low area velocity (10 to 20 standard ft/hr [3 to 6 Nm/hr]), high oxidation efficiencies were achieved in the laboratory, even with these honeycomb samples at the low palladium loading. With a 2-inch (51-mm) honeycomb length, the laboratory oxidation was measured at 97%. The high oxidation percentage would make it

difficult to measure improvements in activity with higher palladium loadings on the honeycomb surfaces.

Additional tests were conducted at a higher synthetic flue gas rate (2 L/min) and with shorter (1/2-inch [13-mm]) honeycomb lengths, so the predicted mercury oxidation percentages would be low enough to quantify the effects of greater palladium loading on the honeycomb. Palladium loadings of one times, three times, and ten times the loading tested at Site 2 were tested. The results of these tests appear in Table 4-25. Also included in this table are predicted results derived from mass transfer equations described above.

Table 4-25
Laboratory Honeycomb Performance Predictions and Actual Results

Palladium Loading	Honeycomb Core Length (in.) [mm]	Area Velocity (std ft/hr) [Nm/hr]	Theoretical Conversion (%)	Actual Conversion (%)	Actual NTU/Predicted NTU
1 ×	0.5 [13]	158 [46]	82	22	0.14
	1 [25]	79 [23]	94	57	0.31
3 ×	0.5 [13]	158 [46]	82	64	0.59
	1 [25]	79 [23]	94	92	0.92
10 ×	0.5 [13]	158 [46]	82	68	0.66
	1 [25]	79 [23]	94	81	0.60

The data in the table for the ratio of actual number of mass transfer units (NTU) to predicted NTU indicate that there is a critical loading on the honeycomb surface, above which additional palladium does not contribute to further mercury oxidation. This loading may correspond with having complete surface coverage by the catalyst. For Pd #1, this critical loading appears to be near three times the original loading, as there is a big improvement in actual relative to theoretical performance going from the original loading to three times that, but no further improvement at ten times the original loading.

At the higher loadings of three times and ten times the original, the actual to predicted NTU ratios are in the same range as they were for the pellet catalyst form in the Site 2 field tests. This further supports the conjecture that the palladium loading on the surface of the Pd #1 pellets was high enough to approach "instantaneous" oxidation of elemental mercury at the pellet surface, but the loading on the honeycomb was limiting the reaction rate. Subsequent Site 3 field testing with the Pd #1 honeycomb catalyst was conducted with three times the original palladium loading.

Effect of Catalyst Temperature on Activity for Elemental Mercury Oxidation

Some laboratory testing concentrated on the effects of simulation gas temperature on mercury oxidation. Specifically, the activity of seven of the most active catalysts at simulated Site 3

conditions (at 300°F [149°C]) was measured at an elevated temperature of 700°F (371°C), which is the nominal temperature at which most SCR units operate for NO$_X$ control.

These tests are of interest because a number of bituminous-coal-fired units with existing FGD systems are now retrofitting SCR systems to lower NO$_X$ emissions. There is great interest as to whether SCR catalysts, operating at 700°F (371°C), will oxidize elemental mercury. If so, plants with SCR and FGD could expect high overall mercury removal. Similarly, there is interest as to whether any of the catalyst materials identified as being active at 300°F (149°C) would also show high activity towards mercury oxidation at 700°F (371°C). If so (and if typical SCR catalysts were less active), if might be cost effective to add a layer of mercury catalyst in an SCR reactor, or to add mercury catalyst material to an SCR catalyst formulation.

The results of these tests are summarized in Table 4-26. The results show that at "Baseline #5" conditions, the carbon-based materials had no activity towards mercury oxidation at 700°F (371°C), but the ash and metal-based catalysts tested all showed high activity. The two palladium-based catalysts and the Fe #1 catalyst showed essentially no effect of temperature, while the activity of Subbituminous Ash #5 and of the SCR catalyst (vanadium/titanium) improved measurably at the higher temperature. The Subbituminous Ash #5 sample result is surprising, since this catalyst is believed to perform similar to the activated carbon materials. Based on the carbon results, we would have expected poor performance of Subbituminous Ash #5 at 700°F (371°C).

Table 4-26
Elemental Mercury Oxidation Percentages at Varied Simulation Gas Temperature and Composition

Sample Name	Baseline #5 Gas Conditions		Gas Condition #6	Gas Condition #7
	300°F (149°C)	700°F (371°C)	700°F (371°C)	700°F (371°C)
Carbon #2	100%	0%	0%	-
Carbon #6	97%	0%	0%	0%
Subbituminous Ash #5	84%	99%	0%	-
Pd #1	92%	96%	91%	92%
Pd #2	95%	94%	92%	-
Fe #1	88%	89%	84%	87%
SCR	57%	94%	95%	90%

The last two columns in the table show oxidation percentages for several of these catalyst materials at alternate, low-sulfur-coal gas conditions. The gas compositions for these additional tests are compared to the "Baseline #5" gas composition in Table 4-27. The gas composition labeled "Condition #6" represents a Powder River Basin coal flue gas, similar to that at Site 2.

Table 4-27
Simulation Gas Conditions for High-Temperature Laboratory Tests

Gas Species	Baseline #5	Condition #6	Condition #7
SO_2	1600 ppm	400 ppm	400 ppm
HCl	50 ppm	2 ppm	50 ppm
NO_X	400 ppm	400 ppm	400 ppm
O_2	6%	6%	6%
CO_2	12%	12%	12%
H_2O	7%	7%	7%

Condition #7 represents that same gas, but at a high HCl concentration similar to that of the bituminous coal, "Baseline #5" gas. This gas was tested to try to separate the HCl and SO_2 concentration effects.

The results in the last two columns in Table 4-26 show the effect of the simulation gas SO_2 concentration and/or HCl concentration on activity. The carbon-based catalysts showed no activity at 700^oF (371^oC) at the alternate gas conditions tested, just as they showed none at the Baseline 5 conditions.

For the metal-based catalysts, the results showed no effect of gas composition on activity at 700^oF (371^oC); all of the results lie within experimental error of the corresponding values for the Baseline #5 composition. Previous results during Phase I of this project had shown low activity for several of these catalysts at 700^oF (371^oC), with a simulation gas that did not contain NO_X. Phase II results at Site 2 conditions but with no HCl in the simulation gas similarly showed low activities at 700^oF (371^oC) for metal-based catalysts. Compared to previous results, these tests suggest that HCl (and NO_X) may play a role in the activity of the metal catalysts at 700^oF (371^oC), but the HCl effect does not seem to be concentration dependent over the range of 2 to 50 ppm. A similar effect of HCl has been seen previously in mercury adsorption and oxidation testing at 300^oF (149^oC).

Subbituminous Ash #5 showed a complete loss of activity at the low sulfur, low HCl Condition #6, compared to 99% oxidation at the high sulfur, high HCl condition of Baseline #5. Subbituminous Ash #5 was not tested at Condition #7, so it is not clear whether it was the lower SO_2 concentration or the lower HCl concentration that affected the activity of the fly ash. Also, as mentioned above, the result for Subbituminous Ash #5 at Baseline #5 conditions and 700^oF (371^oC) is suspect, so the apparent affect of flue gas composition on the activity of this material at 700^oF (371^oC) may just reflect experimental error.

Catalyst Deactivation Rates in Simulated Flue Gas

During Phase II of this project, a portion of the laboratory effort investigated whether the results of longer-term laboratory tests conducted at high area velocity (low catalyst mass in the sand bed) could be used to predict the relative deactivation rates of catalyst materials. There were two areas of interest from these tests. One was whether measurable deactivation rates would result from laboratory tests on simulated flue gas; there was one school of thought that catalyst deactivation in the field was primarily due to the effects of trace species not present in the simulation gas (e.g., selenium at Site 1). The second area of interest was, if deactivation rates measured in the field compared well with field results, laboratory deactivation tests might be a better screening tool than short-term activity tests for selecting catalyst materials for long-term testing in the field.

A number of catalyst deactivation rates tests were conducted in the laboratory using Site 2 simulation gas conditions. The laboratory tests were conducted for time periods ranging from approximately two to eleven days. Deactivation rates were quantified by conducting linear least-squares regressions on the percent oxidation across each bed versus time. The slope of the resulting line was taken as the deactivation rate. Figure 4-6 is an example plot of the laboratory data for Carbon #3. Also shown in the figure is the result of the linear least squares fit to the data.
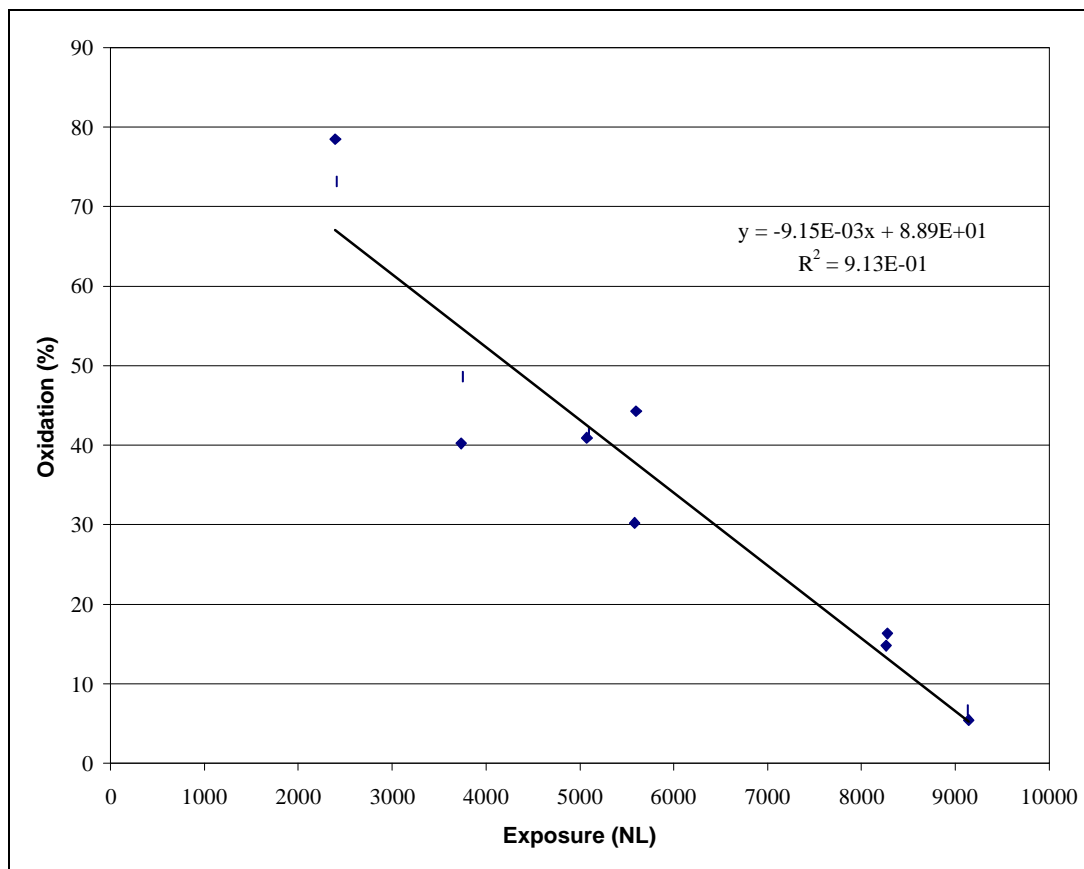

Figure 4-6
Example Laboratory Catalyst Deactivation Data, for Carbon #3

Table 4-28 contains a summary of deactivation rate test results for these laboratory tests, and comparisons to field (Site 2) long-term test results. The deactivation rates have been normalized to account for the fact that these tests were conducted at substantially differing catalyst mass in the sand beds and flue gas (or simulation gas) flow rates. A lower deactivation rate in the table signifies a catalyst that remains active for a longer time. The deactivation rates presented in the table should be interpreted as *order-of-magnitude estimates*.

Table 4-28
Summary of Deactivation Rates Measured for Sand-Bed Catalysts in the Laboratory and Field

Catalyst/Type of Test	Catalyst Loading (mg/[L/min])	Area Velocity (std ft/hr) [Nm/hr]	Observed Catalyst Deactivation Rate (% Oxidation/[mg NL])	Gas Exposure (Total NL)
Carbon #1				
Laboratory	2.5	140 [40]	5×10^{-3}	4,370
Field*	60	6 [2]	8×10^{-6}	62,800
Carbon #3				
Laboratory	2.5	80 [23]	8×10^{-3}	1,950
Laboratory	10	20 [6]	9×10^{-4}	9,140
Field	100	2 [0.6]	2×10^{-6}	635,000
Carbon #6				
Laboratory	5	40 [12]	1×10^{-5}	12,900
Laboratory	10	20 [6]	9×10^{-5}	10,280
Field	100	2 [0.6]	6×10^{-7}	478,000
Pd #1				
Laboratory	50	5000 [1400]	3×10^{-5}	6,480
Laboratory	150	1700 [500]	3×10^{-5}	16,000
Field	1500	160 [46]	3×10^{-9}	583,000

* Field results for Carbon #1 are from the intermediate-length (three-week) short-term test at Site 2; other field results are from the long-term test at Site 2.

The normalized results confirm that Carbon #1 and Carbon #3 deactivate more rapidly than Carbon #6 and Pd #1. This was seen both in laboratory and field results. However, in comparing the deactivation rates for Carbon #6 versus that of Pd #1, the laboratory results were not a good predictor of the relative performance of these two materials. The laboratory deactivation rates

were about the same for these two catalysts, whereas in the field the Pd #1 deactivation rate was two orders of magnitude lower than for the carbon.

Note that for all of the catalysts tested, the laboratory samples tended to deactivate more rapidly than the field samples. The field samples were exposed to flue gas at a much lower area velocity than were the laboratory deactivation beds. Also, the actual flue gas contained trace species not present in the simulation gas. It is not known which of these two factors explain why the catalysts deactivated at differing rates in the laboratory versus in the field.

Because laboratory deactivation tests occupy the laboratory units for long periods of time (typically one to two weeks), the data are somewhat expensive to obtain. Since the laboratory deactivation rates were not observed to correspond directly with field deactivation rates in the comparisons shown above, the value of conducting laboratory deactivation tests came into question. Therefore, the laboratory deactivation test series was suspended after the data summarized in Table 4-28 were collected.

References

1.   Richardson, C. F., et al. "Enhanced Control of Mercury by Wet FGD Systems." Presented at the EPRI-DOE-EPA Combined Utility Air Pollution Control Symposium: The MEGA Symposium, Atlanta, GA, August 16-20, 1999.

2.   *Enhanced Control of Mercury by Wet Flue Gas Desulfurization Systems – Site 1 Results*, EPRI, Palo Alto, CA, and U.S. Department of Energy, Federal Energy Technology Center, Pittsburgh, PA, 1999, TE-113397.

3.   *Enhanced Control of Mercury by Wet Flue Gas Desulfurization Systems – Site 2 Results*, EPRI, Palo Alto, CA, and U.S. Department of Energy, Federal Energy Technology Center, Pittsburgh, PA, 2000. 1000558.

5

PRELIMINARY ECONOMICS FOR A CATALYTIC PROCESS

Preliminary cost estimates have been made for the catalytic process under development, for a 400-MW power plant that has a conventional ESP for particulate control followed by a wet FGD system that treats 100% of the flue gas. Estimates were developed for two sets of plant conditions: one corresponding to a Powder River Basin coal-fired unit similar to Site 2, and one firing a bituminous coal as at Site 3.

The catalyst is Pd #1 on a honeycomb support. The catalyst would be installed immediately downstream of the last field of the ESP, where the flue gas velocity would be about 5 ft/sec. The catalyst life was projected to be three years. Pd #1 saw little or no measurable loss of activity in over five months of testing at Site 2 and after three months of testing at Site 3. It remains to be demonstrated what the actual life of this catalyst will be.

The catalyst loading on the honeycomb cores was assumed to be the value tested in the honeycomb configuration at Site 3. This value was three times higher in palladium loading than was tested in a honeycomb configuration at Site 2.

Powder River Basin Coal Estimate

For the Powder River Basin Coal case, the flue gas was assumed to have a total mercury content of 10 µg/Nm^3, of which 25% is oxidized and 75% is in the elemental form. Although we do not yet have reliable information about the relationship between area velocity and elemental mercury oxidation percentage for Pd #1 on a honeycomb, for these preliminary estimates we used the simple mass transfer model described in Section 3 to predict catalyst performance. The predicted catalyst performance was based on the model prediction for mass transfer, corrected for the observed relationship between the model prediction and actual honeycomb catalyst performance.

The mercury control levels for the catalytic process are based on the assumption that the wet FGD system will achieve 93% removal of the oxidized mercury in the FGD inlet flue gas, and no removal of elemental mercury, which are the values measured at Site 2. The control levels also assume no removal of mercury across the ESP. For these assumptions, the required oxidation percentages across the catalytic process are 81% for the 80% overall mercury removal case, and over 95% for the 90% overall mercury removal case. Based on the model predictions described above, we assumed a 4-inch (102-mm) catalyst depth to result in 81% oxidation and a total of 8-inches (203-mm) of catalyst depth to result in greater than 95% oxidation. These catalyst depths correspond with area velocities of 120 and 60 standard ft/hr, respectively (35 and 17 Nm/hr).

The projected costs for this process were compared to cost estimates for activated carbon injection for mercury control, as presented in a previous EPRI-sponsored paper[1]. In that paper, it was determined that it was more cost effective to retrofit a high-ratio fabric filter downstream of the ESP (i.e., the EPRI COHPAC configuration) when injecting activated carbon for mercury control. Their estimates showed that prohibitively large quantities of carbon were required to achieve high mercury removal efficiency with only the ESP as a gas-solid contactor. That paper presented cost estimates for an 80% mercury removal level, but we used data and cost equations presented in the paper to project costs for a 90% removal level with carbon injection. We also used the same economic factors and plant descriptions used in the EPRI paper in developing preliminary estimates for the catalytic process. These estimates for capital, operating and maintenance (O&M) and levelized costs are compared for 80 and 90% overall mercury removal levels in Table 5-1.

Table 5-1
Preliminary Cost Estimates for the Catalytic Process for Enhancing Mercury Removal by a Wet FGD System Compared to Activated Carbon Injection, for a Plant Firing Powder River Basin Coal

Mercury Removal Process	Catalyst		Carbon Injection/COHPAC	
Overall Hg Removal (%)	80	90	80	90
Total Capital Requirement ($1000; excludes catalyst costs)	$1,949	$1,949	$15,857	$15,911
Levelized Capital Requirement ($1000/yr)	$199	$199	$1,617	$1,623
Total O&M Cost ($1000/yr)	$1,418	$2,833	$1,694	$2,482
Levelized O&M Cost ($1000/yr)	$2,126	$4,250	$2,541	$3,724
Total Levelized Cost ($1000/yr)	$2,325	$4,449	$4,159	$5,347
Percent reduction (relative to carbon injection/COHPAC)	44%	17%	-	-

Note that the EPRI paper did not consider whether the hypothetical power plant had a wet FGD system or any contribution from that FGD system to mercury removal. However, for this comparison, we assumed that downstream of the carbon injection system the mercury remaining would have the same 25% oxidation percentage. Thus, a small fraction of unremoved mercury would be oxidized mercury, and 93% of the oxidized portion would be removed across the FGD system. The carbon injection requirements used in the EPRI paper were adjusted downward to reflect a small contribution of the FGD system to overall mercury removal. Also, note that the capital cost estimates for the catalytic process do not include the cost of the initial catalyst charge. The catalyst cost is instead treated as an O&M expense, since it must be replaced every three years.

The preliminary results in Table 5-1 show that the catalytic process holds some promise for lowering future mercury control costs for power plants that fire Powder River Basin coals and

that have existing FGD systems, particularly to achieve an 80% mercury control level. The catalytic process may also be advantageous for sites where space constraints would make the retrofit of a COHPAC fabric filter difficult.

One plant-specific variable that may affect the success of the catalytic oxidation process is the amount of flue gas bypass around the FGD system. Many FGD systems installed on plants that fire subbituminous or lignite fuels were designed to meet a 1.2 lb/MM Btu SO_2 emissions limit or a 70% SO_2 removal requirement. These designs may incorporate substantial quantities of flue gas bypass (e.g., 20 to 50%). Flue gas that bypasses the FGD system would not realize any oxidized mercury removal. To achieve high mercury removal efficiencies with the catalytic oxidation process, such plants would have to greatly reduce or eliminate flue gas bypass.

However, there are two current economic drivers that encourage the elimination or reduction of flue gas bypass: the market value of SO_2 emissions credits under Phase 2 of Title IV of the 1990 Clean Air Act (CAA) amendments, and financial incentives to co-fire high-sulfur petroleum coke in some geographical areas of the country. In many instances, a utility with an existing FGD system may already have financial incentives to reduce or eliminate flue gas bypass, which would allow high mercury removal efficiencies to be achieved with the catalytic oxidation process. Other issues such as regional haze, New Source review, and $PM_{2.5}$ regulations will cause more plants with FGD to reduce or eliminate flue gas bypass.

Future process development work is needed to substantiate and refine the assumptions made to develop these cost estimates. Longer catalyst life will tend to drive the costs down. Also, less expensive catalysts, such as fly-ash- or carbon-based catalysts, will tend to lower costs.

Bituminous Coal Estimate

For the bituminous coal case, the flue gas was assumed to have the same total mercury content of 10 $\mu g/Nm^3$, but 75% is oxidized while 25% is in the elemental form (as measured at the ESP outlet). Based on data collected from the EPA mercury ICR, for a bituminous coal case we assumed that approximately 25% of the mercury in the flue gas at this site would be removed with the fly ash across the ESP. Note that this percentage is lower than what was measured at Site 3. We also assumed that a net of 90% of any oxidized mercury in the flue gas would be removed by the wet FGD system, which is slightly more conservative than the assumption for the Powder River Basin case.

Based on the assumptions listed above, the oxidation catalyst would have to achieve approximately 25 to 30% oxidation of the elemental mercury in the ESP outlet gas for the plant to achieve 80% overall mercury removal, and 85 to 90% oxidation for the plant to achieve 90% overall mercury removal. Again, for these preliminary estimates we used the mass transfer model to predict catalyst performance. The predicted catalyst performance was based on the model prediction for mass transfer, corrected for the observed relationship between the model prediction and the actual honeycomb catalyst performance at Site 3. It was estimated that a 6-inch (152-mm) catalyst depth would result in 85 to 90% oxidation of the elemental mercury at the ESP outlet and that a 2-inch (51-mm) catalyst depth would result in well over 30% oxidation. However, for the latter case, it was assumed that it would not be feasible or worthwhile to install

catalyst at a bed depth of less than 2 inches (51-mm). These catalyst depths correspond with area velocities of 80 and 240 standard ft/hr (23 and 69 Nm/hr), respectively.

The projected costs for this process were compared to cost estimates for activated carbon injection for mercury control, as presented in same previous EPRI-sponsored paper[1] mentioned above. We assumed the same baseline 25% removal of mercury across the ESP with no carbon injection, and we assumed that downstream of any carbon injection, the ratio of oxidized to elemental mercury would remain 75 to 25%. We also assumed the same 90% removal of oxidized mercury across the FGD system as described above. With these assumptions for the carbon injection cases, about 40% mercury removal upstream of the FGD system would be required for the plant to achieve 80% overall mercury removal, and 70% removal upstream of the FGD for the plant to achieve 90% overall mercury removal.

For our calculations, we first estimated the carbon injection rate required to achieve these mercury removal levels for injection upstream of the existing ESP, then we estimated the carbon injection rate required with a COHPAC pulse-jet fabric filter downstream of the ESP. In the latter case, the removal by the fly ash in the ESP and by carbon in the fabric filter were assumed to be additive, such that the required removal levels at the fabric filter were reduced to 20 and 60%, respectively, for the 80 and 90% overall removal cases.

We also used the same economic factors and plant descriptions used in the EPRI paper in developing preliminary estimates for the catalytic process. These estimates for capital, O&M, and levelized costs are compared for 80 and 90% overall mercury removal levels in Table 5-2.

As in the EPRI paper, in our estimates we found that for carbon injection, it would be more cost effective to retrofit a COHPAC fabric filter as a gas/carbon contactor rather than inject larger quantities of carbon upstream of the ESP. It was somewhat surprising that these preliminary economics showed this to be the case even where the required mercury removal upstream of the FGD system was only 40%.

Note that, as in Table 5-1, the capital cost estimates for the catalytic process in Table 5-2 do not include the cost of the initial catalyst charge. The catalyst cost is instead treated as an O&M expense, since it must be replaced every three years.

The preliminary results in Table 5-2 show that the catalytic process holds some promise for lowering future mercury control costs for bituminous-coal-fired power plants with existing FGD systems, particularly those that do not have space available to retrofit a COHPAC fabric filter between the existing ESP and the FGD system. Future process development work is needed to substantiate and refine the assumptions made to develop these cost estimates. Longer catalyst life will tend to drive the costs down. Also, less expensive catalysts, such as fly-ash-based or carbon-based catalysts, will tend to lower costs.

Table 5-2
Preliminary Cost Estimates for the Catalytic Process for Enhancing Mercury Removal by a Wet FGD System, Compared to Activated Carbon Injection

Mercury Removal Process	Catalyst		Carbon Injection/COHPAC	
Overall Hg Removal (%)	80	90	80	90
Required Elemental Mercury Oxidation Across Catalyst (%)	26	87	-	-
Required Mercury Removal Across Fabric Filter (%)	-	-	18	59
Total Capital Requirement ($1000; excludes catalyst costs)	$1,949	$1,949	$15,820	$15,837
Levelized Capital Requirement ($1000/yr)	$199	$199	$1,614	$1,615
Total O&M Cost ($1000/yr)	$710	$2,125	$1,154	$1,406
Levelized O&M Cost ($1000/yr)	$1,064	$3,188	$1,731	$2,109
Total Levelized Cost ($1000/yr)	$1,263	$3,387	$3,345	$3,725
Percent reduction (relative to carbon injection/COHPAC)	62%	9%	-	-

References

1.   Meserole, F.B., et al. "Estimating Electric Utility Mercury Control Costs Using Sorbent Injection." Presented at the EPRI-DOE-EPA Combined Utility Air Pollution Control Symposium: The MEGA Symposium, Atlanta, GA, August 16-20, 1999.

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CONCLUSIONS AND RECOMMENDATIONS

Sand bed reactor tests conducted at three sites during this project have shown that there are a number of materials that retain high activity towards elemental mercury oxidation in flue gas over the periods tested, up to six months. Depending on the site, these active materials include metals such as Pd #1, carbons such as Carbon #6, and ashes such as Subbituminous Ash #5. No one material remained active over the test duration at all three sites, but this comparison is confounded by extraordinary events (e.g., a low temperature excursion in the long-term test apparatus at Site 1).

The project did not include fundamental research to determine mercury oxidation mechanisms on the catalyst surfaces. However, the differences in performance of catalyst materials between the three sites appear to be due to variations in flue gas conditions. Laboratory testing suggests that flue gas species such as SO_2, SO_3, HCl and NO_X may impact catalyst oxidation activity and/or deactivation rates. The laboratory studies also suggest that trace species such as selenium in the flue gas may play a role in catalyst deactivation.

Laboratory results also indicate that the activities of sand bed materials are, in general, readily restored by regeneration with nitrogen or CO_2 at temperatures up to 700^oF (371^oC). Sulfur and selenium are the primary species that desorb from the catalysts upon regeneration, but it is not certain that catalyst activity is tied to the presence or absence of these species on catalyst surfaces. It is also undetermined as to how long the regenerated materials will remain active relative to the activity of virgin materials.

The sand bed reactor field results appear to successfully predict activity in commercially available catalyst forms. Sand bed reactor results were used to select the Pd #1 material for testing in pellet and/or honeycomb forms at Sites 2 and 3, and high activities were also measured for those catalyst forms. Short-term commercial catalyst form tests showed that for the Pd #1 material, high elemental mercury oxidation percentages (70% and greater) could be achieved at area velocity values much higher than in typical flue gas SCR applications. SCR is the most prevalent example of a catalytic process applied to coal flue gases. Since the catalytic mercury oxidation process would be applied to flue gas downstream of the particulate control device but upstream of an FGD system, the flue gas treated would be relatively particulate free. This should allow the use of honeycomb catalysts with a relatively close pitch (e.g., smaller cell diameters, and greater geometric surface area per cubic foot of honeycomb) compared to typical SCR applications. The substantially higher area velocities, tighter honeycomb pitch, and lower gas temperatures (300^oF vs. 700^oF [149^oC vs (371^oC)]) in combination mean that a catalytic mercury oxidation reactor could be substantially smaller than a typical SCR application (e.g., less than $1/10^{th}$ the size of an SCR reactor).

Preliminary process cost estimates indicate that a catalytic mercury oxidation process could be a less expensive approach for achieving 80% to 90% overall mercury control by plants equipped with FGD than employing carbon injection, which is currently perceived to be the most commercially available mercury control technology. These estimates are based on Pd #1 catalyst, an assumed three-year catalyst life, and catalyst replacement at the end of each three-year period. The ability to use lower cost (than palladium) catalyst materials, longer catalyst life than three years, and/or the ability to regenerate rather than replace catalysts could improve on the economics of this process.

Flue gas characterization efforts conducted as part of this project have shown that flue gas mercury concentrations can vary widely at a given power plant, in most cases due to variations in coal sources and/or fuel quality variations within a single mine. This variability underlines an advantage of a catalyst-based system for enhancing mercury removal by FGD systems: the ability to achieve high removal efficiencies is relatively insensitive to mercury concentrations in the flue gas. In contrast, carbon injection technology requires monitoring of mercury concentrations to ensure optimum performance. Injecting at too low a rate for the current flue gas mercury concentration could lead to poor removal, while injecting at too high a rate will result in poor carbon utilization.

Limitations of the Current Results

Although the field and laboratory sand bed reactor tests conducted during this project were quite successful in advancing the state of the proposed mercury catalytic oxidation technology, there are a number of limitations identified in the sand-bed reactor testing concept, and a number of unknowns that remain to be addressed.

One limitation is due to the small scale of the current testing. At such a small scale, wall and edge effects can overwhelm results from the long-term test apparatus. An example is the testing at Site 3, where the flue gas flowing through the test apparatus was measured to contain very little elemental mercury while the bulk flue gas in the FGD inlet duct was measured to contain normal levels, of approximately 4 $\mu g/Nm^3$. This was speculated to have been caused by a very small amount of fly ash buildup within the long-term test apparatus, which lead to elemental mercury oxidation and/or adsorption. In a larger test apparatus, with a much lower surface area to volume ratio, such fly ash effects would have been negligible.

Another limitation of the size of the current project has been the inability to measure the impacts of catalyst materials on other species in the flue gas, as the gas flow through the apparatus was generally too low to analyze by standard methods. For example, will materials that catalyze the oxidation of elemental mercury in flue gas also catalyze NO or SO_2 to go to higher oxidation states (e.g., NO_2 or SO_3, respectively)? Further oxidation of either of these species would be undesirable, and would likely make the mercury oxidation technology less viable.

At the beginning of this project, there was no standard method for measuring and speciating mercury concentrations in coal flue gases. Over the period of performance, the U.S. EPA announced that they favored the draft Ontario Hydro method for making such measurements, and required the use of that method for their ICR program. The EPRI semi-continuous mercury

analyzer used in the long-term sand-bed test apparatus on this project was very useful for measuring catalyst performance on a near real time basis. However, the test apparatus did not have provisions for confirming catalyst performance with the draft Ontario Hydro method. Thus, the mercury oxidation results from this project have not been validated with an "approved" measurement and speciation method.

The ability to use sand-bed reactor results to select catalyst materials for testing in commercial forms was demonstrated by successful testing of Pd #1 in pellet and honeycomb forms. However, the ability to apply other materials such as carbons or fly ashes to honeycomb substrates to produce active catalysts was not demonstrated. While organizations such as Corning Incorporated and the Illinois State Geological Survey have reportedly developed technologies for applying such materials to honeycomb substrates, catalysts prepared in such a manner were not tested as part of this project.

The current project has demonstrated that some materials remained active for elemental mercury oxidation for periods of up to six months. However, a successful process based on this catalytic oxidation technology will likely require that catalysts remain active for periods of several years. Longer-term testing (e.g., one or more years' duration) is required to determine whether a catalyst-based mercury removal technology will be economically viable.

Furthermore, catalyst regeneration could have a major impact on the economics of such a process. While laboratory regeneration testing indicated that regeneration gas temperatures on the order of 700°F (371°C) are most effective, it remains to be determined what regeneration gas composition will be required. Nitrogen and CO_2 were shown to be effective as regeneration gases, but it would be desirable to determine if oxygen-containing gases, such as air or clean, natural-gas-derived flue gases, could be used for this purpose. The latter might allow in situ regeneration to be cost effectively implemented (e.g., natural gas burners used to produce regeneration gases in situ in out-of-service catalytic reactor sections).

More study is needed to determine the activity of regenerated catalysts over time compared to that of virgin materials, and to determine the number of regeneration cycles a catalyst may be able to sustain. Both of these pieces of information will be important for determining potential process economics.

Recommendations

Based on the successes of the current project in establishing that a number of materials remain active towards elemental mercury oxidation in flue gases for extended periods, we recommend continued development of the proposed catalytic process. However, recognizing some of the limitations associated with testing at the small scale of the current program, we recommend that subsequent development work be conducted at pilot scale (flue gas from at least 1 MW of generating capacity).

The pilot-scale testing should be conducted with the most likely catalyst form for a commercial application of this technology, coated or extruded honeycomb structures. Because a number of potential catalyst materials have been identified, the pilot unit should have provisions to test a

number of catalysts in parallel at any one time. Catalysts tested should include Pd #1 as well as carbons and/or fly ashes applied to honeycomb substrates, such as those prepared by Corning Incorporated or the Illinois State Geological Survey. The pilot unit should contain an array of at least four (two by two) standard honeycomb blocks, such as would be used in greater numbers to build up a full-scale catalyst installation.

Pilot testing should be conducted for at least a year at a given location, with even longer duration being desirable. The pilot unit should have provisions for in situ catalyst regeneration, if feasible, so that the activity of regeneration material can be measured over time for comparison with that of virgin material. The feasibility for in situ regeneration can first be evaluated in the laboratory, using gases that simulate flue gases from clean fuels such as natural gas or propane. If the oxygen content of such flue gases proves detrimental to regeneration some catalyst forms (e.g., carbons) it may be necessary to conduct off-site regeneration in a more inert gas such as nitrogen or CO_2.

Routine pilot unit mercury oxidation data can be monitored with the EPRI semi-continuous mercury analyzer as was used in the current project. However, catalyst performance should be periodically confirmed with manual sampling by the draft Ontario Hydro method.

Each catalyst should also be periodically monitored to determine effects on other flue gas species. In particular, the concentrations of NO_2 and SO_3 upstream and downstream of each catalyst bed should be measured.

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